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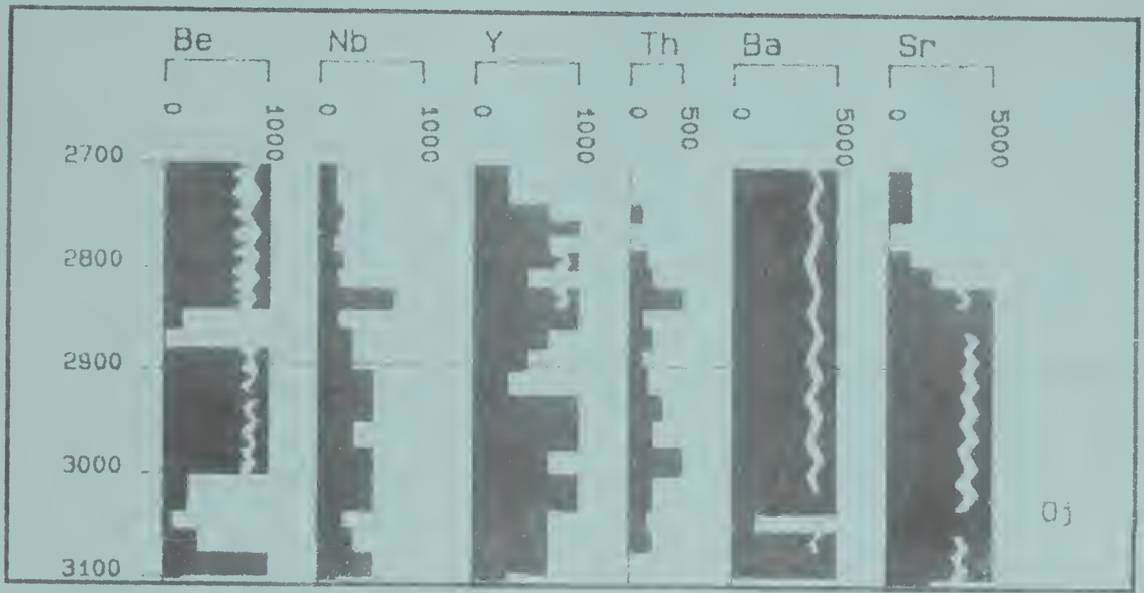

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Subsurface geochemical investigation in western and southern Illinois: a pilot study

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FIGURES

TABLES

ABSTRACT

A pilot geochemical study of insoluble residues of subsurface Paleozoic carbonate rocks from drill holes in western and southern Illinois has been completed by the Illinois State Geological Survey and the U.S. Geological Survey. Geochemical maps and bar graphs based on spectrographic analyses show stratigraphic distribution and abundance of selected elements, reveal subsurface regions of anomalously high subsurface metal values, permit speculation about possible regional target areas, and suggest specific concepts and models of mineral occurrence that should be tested. Results also suggest new avenues of research on ore-forming processes and metal and sulfur sources in the Illinois Basin.

Zinc is the most abundant metal in insoluble residues from Ordovician, Silurian, Devonian, and Mississippian carbonate rocks. Lead is the most abundant metal in insoluble residues of Cambrian carbonates (as it is in southern Missouri). Anomalously high amounts of six metals (Zn, Pb, Cu, Mo, Ni, Ag) and barium and strontium are present in southern Illinois; zinc predominates in western Illinois.

At least four different types of ore deposit models, based on geological and geochemical characteristics of known mining districts, should be considered in western and southern Illinois: (1) Ordovician-hosted and possible Devonian-hosted zinc-lead deposits in west-central and northwestern Illinois similar to those in the Upper Mississippi Valley Zinc-Lead District; (2) new Mississippian-hosted fluorite, barite, zinc, and lead deposits in southwestern Illinois similar to known deposits farther east in the Illinois-Kentucky Fluorspar District; (3) Cambrian-hosted lead-rich base metal deposits similar to those in the world-class Southeast Missouri Lead District; and (4) cryptovolcanic breccia-hosted deposits (Be, Nb, Y, REE, Th, Ba, F) similar to those known to occur at Hicks Dome.

INTRODUCTION

The Illinois State Geological Survey (ISGS) and the U.S. Geological Survey (USGS) have completed a pilot geochemical study of insoluble residues of subsurface Paleozoic carbonate rocks from drill holes in western and southern Illinois. Regional subsurface geochemical studies are an integral part of the USGS program for assessing the mineral resource potential of platform carbonates in the central region of the United States. They have also become an integral part of mineral resource assessment in Illinois, where much of the land is flat to gently rolling agricultural land, outcrops are few, and known favorable host rocks are at depths ranging from a few tens of meters to more than one kilometer. Traditional surface geochemical techniques for evaluating the potential for concealed or undiscovered mineral deposits are of little use in such areas.

Geochemical studies in the Rolla and Springfield 1° x 2° Quadrangles in Missouri (Erickson and others, 1978, 1979, 1985) indicated that insoluble residues of carbonate rocks are a useful and informative

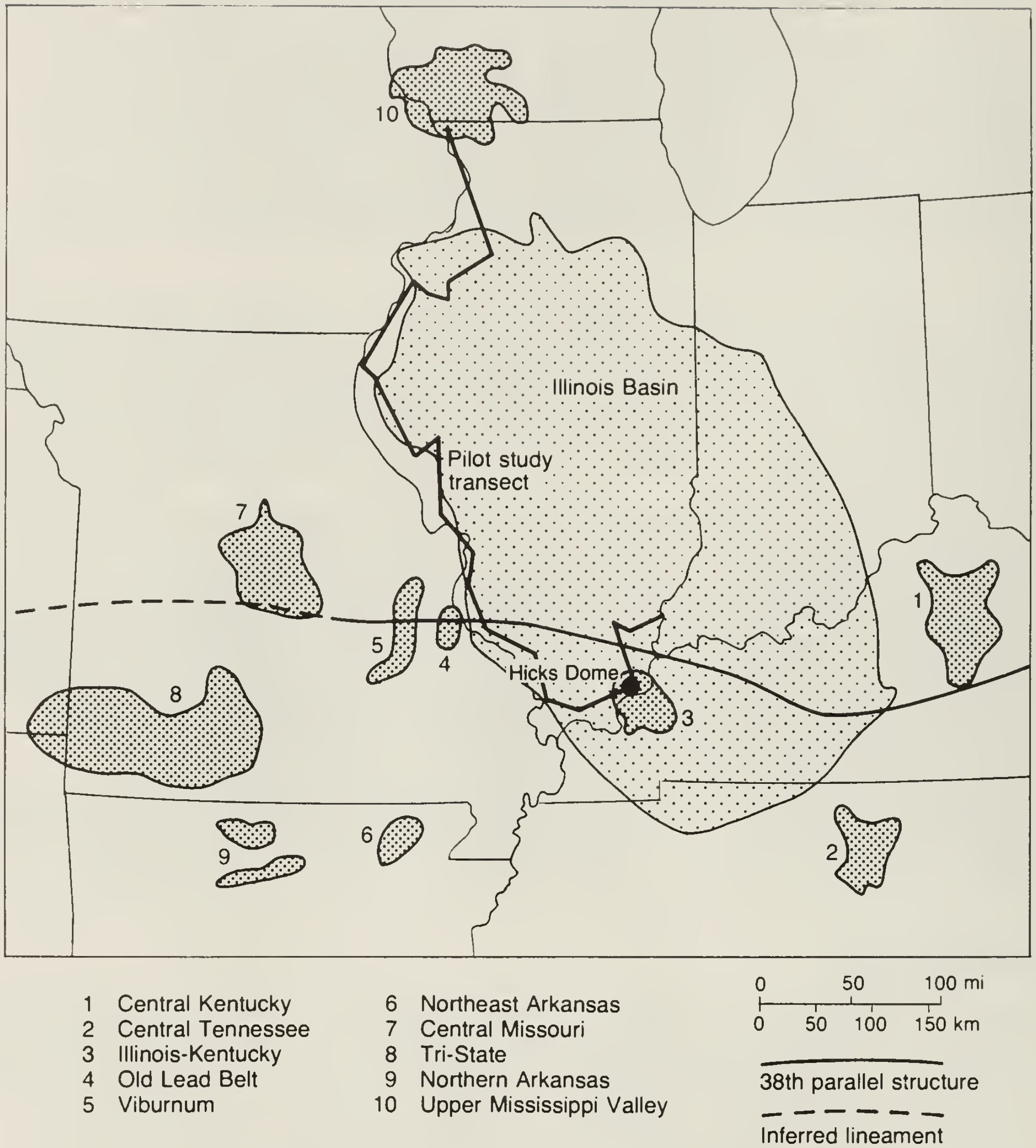


Figure 1 Relationship of pilot study transect with respect to Mississippi Valley-type lead-zinc deposits and Illinois-Kentucky Fluorspar District (mineral districts modified from Heyl, 1972).

geochemical sample medium in a carbonate environment. Spectrographic and chemical analyses of residues from apparently barren whole rocks permit detection of trace amounts of elements not detected by conventional whole-rock analytical methods. The resulting map patterns of distributions and abundances of trace elements permit distinction between intrinsic and epigenetic suites of elements, recognition of rock units through which metal-bearing fluids have passed, and delineation of regional mineral trends. The geochemical maps of the Rolla and Springfield Quadrangles, based on analyses of insoluble residue samples from regionally spaced drill holes, were part of the total body of geological data used to assess the metallic mineral-resource potential of those quadrangles (Pratt, 1981; Martin and Pratt, 1985). The same type of geochemical study is being extended to the Harrison (MO and AR) and Joplin (MO and KS) 1° x 2° Quadrangles.

The purpose of the Illinois pilot study was to (1) determine whether or not geochemical analyses of insoluble residues would be a useful method for assessing the mineral resource potential in Paleozoic carbonate rocks in and on the flanks of the Illinois Basin, and (2) compare the geochemical data obtained in this study with geochemical data from the Upper Mississippi Valley Zinc-Lead District, the Illinois-Kentucky Fluorspar District, and the Southeast Missouri Lead District (fig. 1). In addition, we wanted to determine if the insoluble residue method would be applicable to a long-range ISGS program designed to establish a subsurface geochemical database on a state-wide network of geologic cross sections. Acquisition of such a database is essential for achieving a better understanding of the mineral resource base and issues related to the environment, groundwater quality, and geologic hazards in Illinois. Residue-based subsurface geochemical studies are currently underway in the Paducah 1° X 2° Quadrangle in southernmost Illinois and adjacent Missouri and Kentucky and Indiana, as part of a Conterminous U.S. Mineral Assessment Program (CUSMAP) being conducted by the USGS and the four state surveys.

METHOD OF STUDY

Insoluble residue samples (material remaining after rock samples were dissolved in a 5:1 HCl solution) from 30 drill holes on a north-south transect that extends from the Upper Mississippi Valley Zinc-Lead District to the Illinois-Kentucky Fluorspar District (fig. 2) were selected for the pilot study from the sample library of the ISGS. None of the holes is company confidential and none intersects economically significant mineralized ground, stipulations similar to those applied to sample selection for the Rolla, MO 1° x 2° Quadrangle.

Most samples are a composite of a 10-foot interval; some are composites of thicker intervals (15 ft to 80 ft), depending on the original sample interval and on the amount of sample material available for analysis. Samples of thick shale intervals, such as the New Albany Shale Group of late Devonian and early Mississippian age

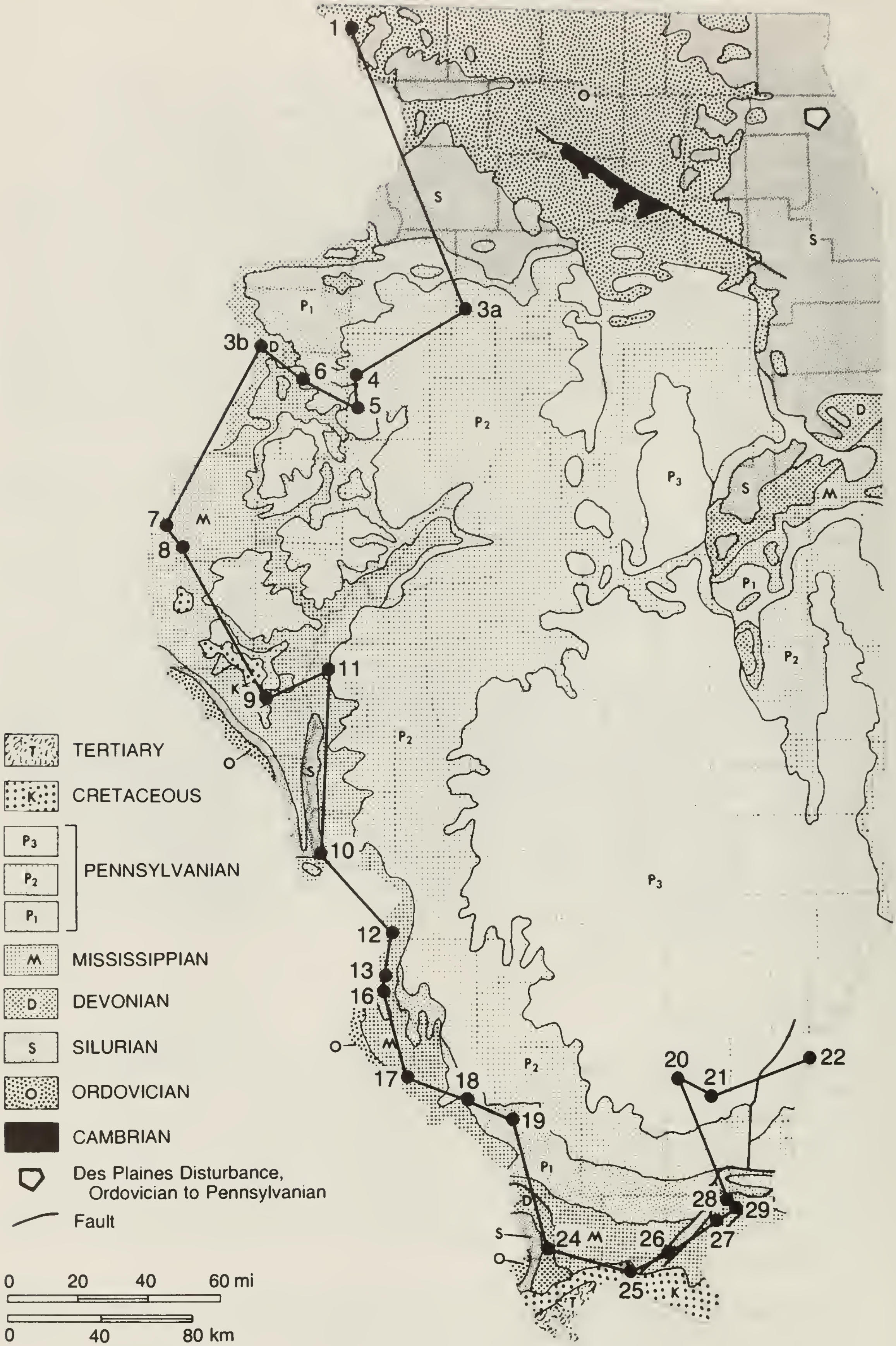


Figure 2 Wells from which insoluble residue samples were taken.

and the Maquoketa Shale Group of Cincinnatian (late Ordovician) age, and thick sandstone intervals such as the St. Peter Sandstone of Champlainian (middle Ordovician) age, were not analyzed. Core samples were available from two holes. All other samples were cuttings from churn- or rotary-drilled oil tests and water wells. The samples were examined with a binocular microscope and described prior to analysis.

Drill cuttings commonly contain fragments of drill steel; many samples contain caved material, particularly shale fragments; a few samples contain paint flakes, solder, or drilling fluid additives. Nevertheless, analysis of samples from which most of the extraneous material was removed provided informative geochemical distribution and abundance patterns. Drill holes I-14 and I-15 were eliminated from the pilot study because of severe contamination problems, and drill hole I-2 was dropped because there were not enough samples available for analysis; drill hole I-23, a deep basin test to basement with more than 700 samples, could not be analyzed, given the time constraints of the pilot study.

Table 1 provides information on the drill holes analyzed in this study (transect hole number, GIS-API number, sample set or core number, well name, and location) to permit correlation with descriptive logs on file at the ISGS. Strata penetrated and intervals analyzed in each drill hole are shown in figure 3.

Each sample was analyzed semiquantitatively for 31 elements by a six-step D.C.-arc optical-emission spectrographic method (Grimes and Maranzino, 1968). Bar graphs showing the distribution and abundances in parts per million of metals within each drill hole are included in the appendix. The stratigraphic names and boundaries used on the bar graphs follow standard ISGS nomenclature and practice (Willman et al., 1975).

Summarized analytical results for each drill hole are plotted for the ratio of zinc to zinc + lead + copper (fig. 4), for each geologic system (figs. 5 thru 8), and for individual metals (figs. 9 thru 14). Element values are reported in anomalous metal feet (AMF) as defined in the Rolla, MO 1° x 2° Quadrangle (Erickson and others, 1978). AMF is a reporting unit derived by normalizing the ratio of a reported anomalous metal content to the minimum anomalous metal content multiplied by the length of the sample interval in feet. The minimum anomalous metal contents of insoluble residues are the same as those established for the Rolla, MO Quadrangle, and were judged to be applicable by inspection of the Illinois data and comparison to the Rolla data. They are, in parts per million: As, 200; Zn, 200; Pb, 100; Cu, 100; Ni, 70; Co, 30; Mo, 10; and Ag, 1. (For elements abbreviations, see appendix p. 28.) Thus, reported values of 500 ppm Pb and 3 ppm Ag for a 10-foot sample interval normalize to 50 AMF of Pb and 30 AMF of Ag. The AMF can be summed for an entire drill hole, for each formation, or for individual metals.

The geochemical patterns (figs. 4-14, and 16) result from simple form lines drawn to call attention to clusters of high AMF values. The patterns have no geographic validity and are not meant to imply a continuum of AMF values between the widely spaced drill holes.

The relative abundance of Zn, Pb, Cu, Mo, Ni, Ag, and As (in AMF) for each geologic system (fig. 15), the median content of each metal for each geologic system (table 2), and the abundance of each metal (in AMF) for each drill hole (table 3) also aid interpretation of the analytical data.

RESULTS

Zinc is clearly the most abundant metal in the insoluble residue samples analyzed in the pilot study (figs. 4 and 15). The ratio of Zn to Zn + Pb + Cu (fig. 4) is 0.9 or greater in 11 of the 26 drill holes, and 0.5 or greater in 22 of the 26 holes. Figure 15 shows the relative abundance of metals for each geologic system and emphasizes the zinc-rich character of Ordovician, Silurian, Devonian, and Mississippian samples. Analyses of Silurian and Devonian residues are not differentiated. Lead is the most abundant metal in insoluble residues of Cambrian carbonates, as it is in Cambrian carbonates in the Rolla and Springfield, MO 1° by 2° Quadrangles (table 2 and fig. 15).

Metal distribution by geologic system

Cambrian System. Figure 5 shows the location and total AMF content of insoluble residue samples in carbonate rocks of Cambrian age. Thirteen drill holes in the study bottom in or penetrate Cambrian rocks. Most Cambrian penetrations are in the northern half of the transect, where the depth to Cambrian strata is much less than in southern Illinois. Residues from Cambrian carbonates are notably zinc-poor (table 2 and fig. 15); however, when anomalous amounts of metals are found, the suite tends to be Pb-rich, with significant amounts of Cu, Mo, As, Ni, and Ag. Metal content in Cambrian carbonate rocks increases to the south. Two deep drill holes that penetrate Cambrian rocks in southern Illinois (I-21 and I-24) have high total AMF contents and an extensive metal suite (Pb, Zn, Cu, Mo, Ni, Ag). This Pb-rich suite is similar to the metal suite in the Cambrian-hosted Southeast Missouri Lead District (Viburnum Trend and Old Lead Belt) (Erickson and others, 1978, 1979, and 1985). Unlike samples from southeast Missouri, several samples from the basal part of the Cambrian section (drill hole I-21) in the deepest part of the Illinois Basin contain 5,000 ppm or more barium (appendix, I-21). The unusually high zinc content (10,000 ppm or greater) in drill hole I-24 in Union County in the Croixian (upper Cambrian) Eau Claire formation, equivalent to the Bonneterre Formation of Missouri, was also unexpected; similar anomalously high values were not encountered in the Rolla or Springfield Quadrangles. The abundance of metals deep in the Illinois Basin (appendix, I-21) has important implications regarding the genesis of carbonate-hosted mineral deposits in the midcontinent.

Table 1 Drill holes evaluated for pilot study.

Drillhole no.	GIS-API no.	Sample set or core no.	Well name	County	Location Sec.	T.	R.
I-1	085 - 346	SS239	Thorne - Galena City #2	Jo Daviess	24	28N	1W
I-2*	195 - 46	SS57	Wilson - Morrison City #1	Whiteside	18	21N	5E
I-3A	073 - 521	SS613	Thorpe - Kewanee City #2	Henry	33	15N	5E
I-3B	131 - 172	C3534 SS30473 31725	Kelly - Fullerton #1	Mercer	19	13N	4W
I-4	095 - 11	SS771	Thorpe - Galesburg City	Knox	16	11N	1E
I-5	095 - 585	SS703	Thorpe - Abingdon City #2	Knox	33	10N	1E
I-6	187 - 233	SS544	Geiger - Monmouth City #2	Warren	29	11N	2W
I-7	067 - 235	SS1182	Walmar - Mitze #1	Hancock	13	4N	9W
I-8	067 - 157	SS11030	Herndon - Laffey #1	Hancock	17	3N	7W
I-9	149 - 205	SS17625	Panhandle Eastern - Mumford #1-21	Pike	21	5S	4W
I-10	083 - 178	SS17624	Kerwin - Legate #1	Jersey	2	6N	13W
I-11	171 - 97	SS971	Texas - Mueller #1	Scott	2	15N	13W
I-12	119 - 1321	SS226	Commonwealth Steel Co.	Madison	24	3N	10W
I-13	163 - 1591	SS723	Lockwood - Dryoff #1	St. Clair	26	1N	10W
I-14**	163 - 30	SS620	Mason, Wagner et al - Gundlach #1	St. Clair	24	1N	8W
I-15**	163 - 312	SS702	Mason et al - Funk #1	St. Clair	14	1S	7W
I-16	133 - 28	C280D SS22156	Miss. River Fuel - Theobald #A-15	Monroe	35	1S	10W
I-17	157 - 1473	SS2974	Ames - Nicholson #1	Randolph	12	5S	9W
I-18	157 - 635	SS2995	Badger - Schroeder #1	Randolph	29	6S	6W
I-19	077 - 1035	SS206	Mid Egypt - Lange #4	Jackson	15	7S	4W
I-20	065 - 1587	C2488	Howard and Howell - Leslie #1	Hamilton	22	5S	5E
I-21	065 - 3450	SS52094	Texaco - Cuppy #1	Hamilton	6	6S	7E
I-22	193 - 4694	C2740	Superior - Ford #C-17	White	27	4S	14W
I-23+	191 - 7731	SS55004	Union of California - Cisne Comm. #1	Wayne	3	1S	7E
I-24	181 - 106	SS55458	Humble - Pickle #1	Union	21	13S	2W
I-25	127 - 32	SS1396	Kahle et al - Harvick	Massac	23	14S	3E
I-26	151 - 106	SS21296	Wilson - Okerson #1	Pope	32	13S	5E
I-27	151 - 145	C3201	Meisner - Belt #1	Pope	9	12S	7E
I-28	069 - 270	C2522	USBM - Knox and Yingling K-4	Hardin	11	11S	7E
I-29	069 - 43	SS1670	Northern Ordnance (Maretta) - Fricker #1	Hardin	30	11S	8E

* Analyses eliminated due to small number of samples
** Analyses eliminated due to contamination
\+ Not analyzed due to time contstraints

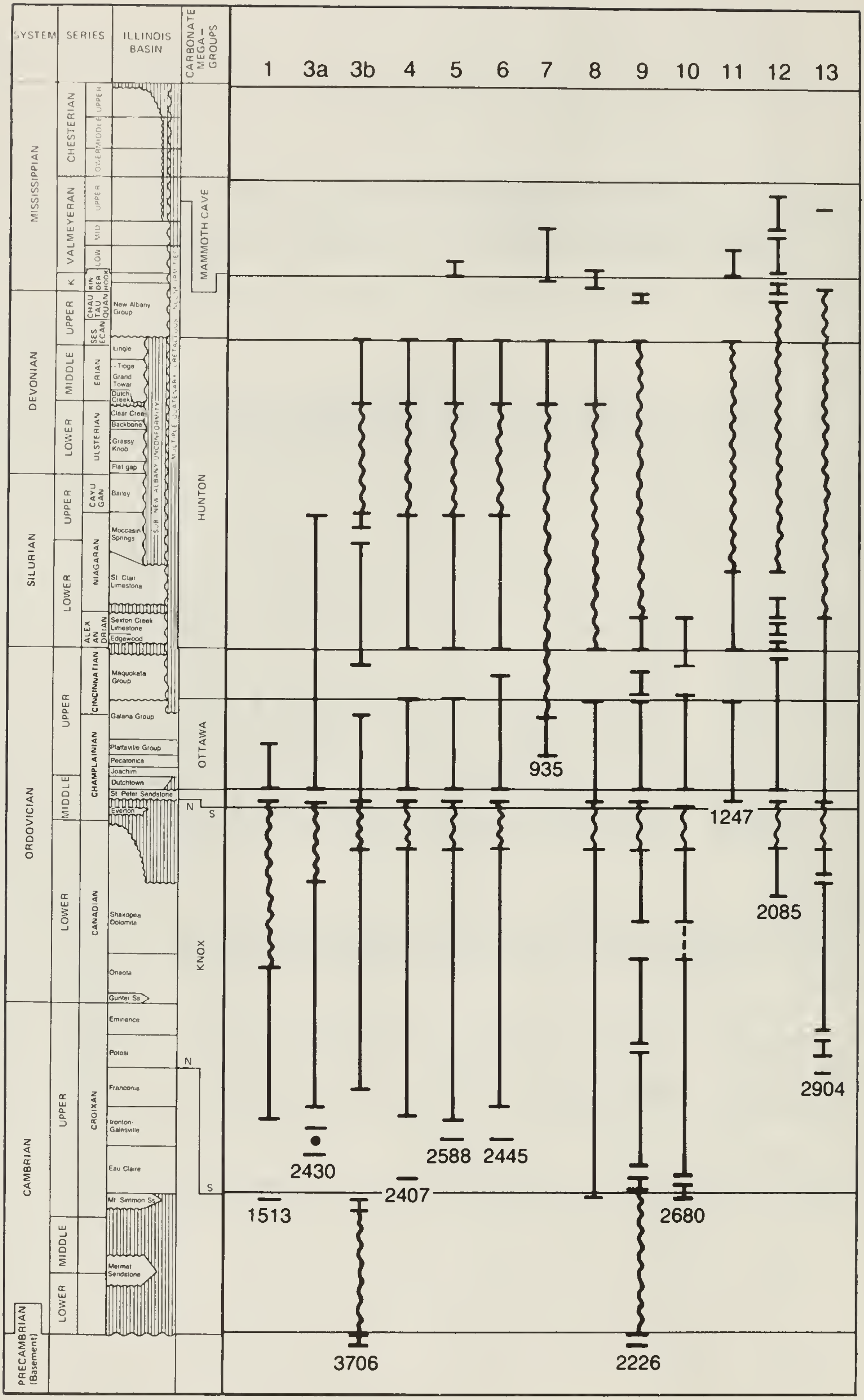
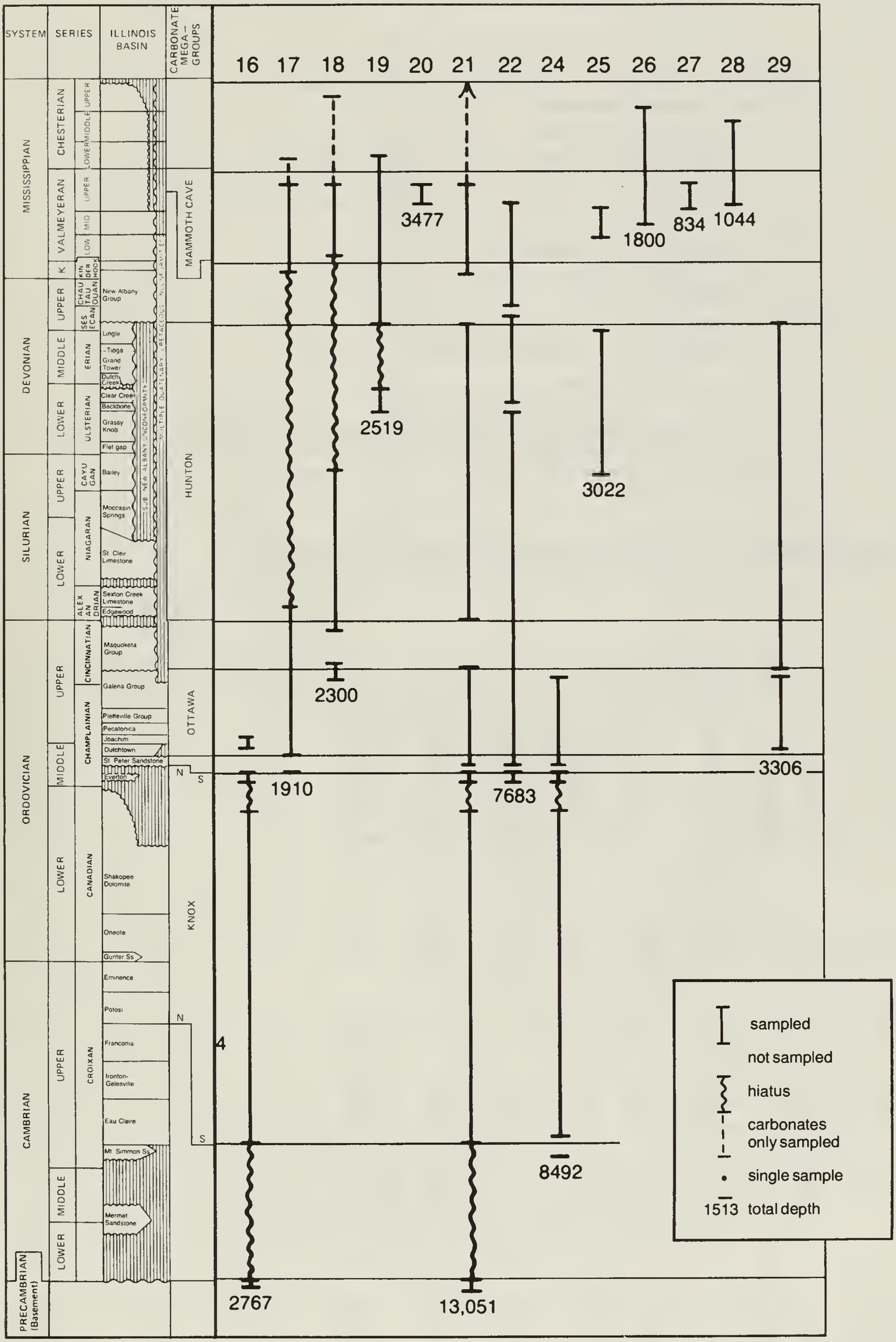


Figure 3 Strata penetrated and intervals analyzed for pilot study



(includes generalized stratigraphic column of Illinois Basin).

Table 2 Median metal content (in AMF) of insoluble residue samples.

	Total metals	Zn	Pb	Cu	Mo	Ni	Ag
Illinois pilot study							
Mississippian	740	500	20	30	85	75	0
Devonian and Silurian	545	255	0	15	50	45	0
Ordovician	2950	1550	125	145	155	55	0
Cambrian	595	15	45*	130	0	30	0
All samples	5125	4140	195	150	405	155	60
Rolla 1, x 2, Quadrangle, MO							
Cambrian Bonneterre Formation	1155	10	300	40	30	30	70
Springfield 1, x 2, Quadrangle, MO							
Post-Bonneterre Cambrian	2155	70	300	460	260	215	65

*Pb median may be low. All samples that contained the suite Pb, Sb, and Sn were assumed to be contaminated (solder?) and Pb values were eliminated from statistical calculations.

Table 3 Metal content (in AMF) of insoluble residue samples from drill holes.

Drill hole	Ag	As	Cu	Mo	Ni	Pb	Zn	Total	No. of samples with >5000 ppm Ba	No. of samples with >5000 ppm Sr	Principal host(s)
I-1	0	10	70	0	155	0	1550	1785	0	0	Ottawa Megagroup
I-3A	0	0	150	115	640	90	4165	5160	0	0	Ottawa Megagroup
I-3B	0	0	595	60	100	2840	1530	5125	0	0	Ottawa Megagroup
I-4	0	0	190	140	205	355	4550	5440	0	0	Ottawa Megagroup
I-5	80	20	585	480	595	560	6625	8945	1	0	Ottawa Megagroup
I-6	0	0	7350	170	335	225	16,670	24,905	0	0	Ottawa Megagroup
I-7	0	10	95	145	10	165	4555	4880	0	0	Devonian System
I-8	140	190	395	985	130	60	2635	4935	1	0	Ottawa Megagroup
I-9	0	175	580	755	320	195	905	2930	0	0	Ottawa Megagroup Cambrian System
I-10	0	30	950	355	20	405	2680	4440	0	0	Ottawa Megagroup Cambrian
I-11	200	0	85	80	85	50	5500	6000	0	0	Ottawa Megagroup
I-12	0	30	50	280	80	20	1845	2305	1	0	Ottawa Megagroup
I-13	100	10	60	425	115	200	2585	3495	1	0	Ottawa Megagroup Mississippian
I-16	385	35	400	955	245	2595	0	4615	12	2	Cambrian
I-17	0	0	1005	405	75	0	2365	3850	3	0	Mississippian Ottawa Megagroup
I-18	285	0	140	545	800	665	11,105	13,540	0	0	Mississippian
I-19	20	15	120	610	130	35	6770	7700	2	1	Mississippian
I-20	0	0	50	15	20	0	185	270	2	1	No specific host
I-21	1200	100	3130	12,750	1245	13,550	4170	36,145	13	101	Cambrian Mississippian Canadian Series
I-22	910	240	1240	3495	1470	130	4140	12,495	8	62	Mississippian Silurian and Devonian Ottawa Megagroup
I-24	7900	735	1465	8845	350	15,875	5495	40,665	3	28	Cambrian Canadian Series
I-25	40	0	0	40	60	60	565	775	0	2	Mississippian
I-26	60	0	50	375	405	355	7265	8510	1	0	Mississippian
I-27	100	60	35	640	90	20	50	1050	1	8	Mississippian
I-28	75	85	5	85	170	5	40	465	6	0	No specific host
I-29	105	105	615	615	300	2575	6120	10,435	29	16	Ottawa Megagroup

Ordovician System. Figure 6 shows the location and total AMF contents of insoluble residues of carbonate rocks of Ordovician age. Nineteen drill holes either bottom in or penetrate Ordovician rocks. The highest metal values occur in Ottawa Limestone Megagroup strata (Platteville and Galena Groups) in west-central Illinois; the pattern extends northward towards Iowa and may represent a southward extension of the Upper Mississippi Valley Zinc-Lead District in Wisconsin, Iowa, and northern Illinois. Zinc is the most abundant metal in the Ordovician of west-central Illinois (table 2). High lead contents in drill hole I-3B in Mercer County (fig. 10) and high copper contents in drill hole I-6 in Warren County (fig. 11) are associated with the zinc. The underlying formations of the Canadian Series (Oneota Dolomite and Shakopee Dolomite or their equivalents) are almost devoid of anomalous amounts of metal in this area.

The analyses of Ordovician insoluble residue samples from drill holes in southern Illinois reveal metal abundances much different from Ordovician metal abundances in drill holes on the remainder of the transect. In southern Illinois zinc contributes less than 10 percent to the total AMF content. Small amounts of molybdenum contribute 77 percent of the total AMF value for drill hole I-21; Cu contributes 76 percent to drill hole I-22; and Pb and Mo contribute 57 and 29 percent respectively to drill hole I-24. Analytical results for Ordovician strata in drill hole I-29 at Hicks Dome in Hardin County are discussed in a separate section of this report.

Silurian and Devonian Systems. Figure 7 shows the location and total AMF contents of insoluble residues of carbonate rocks of Silurian and Devonian age included in the Hunton Limestone Megagroup. Seventeen drill holes in the study penetrate Silurian and/or Devonian strata. The highest metal values occur in west-central and southern Illinois. Zinc is the most abundant metal in both areas. The high zinc content in drill hole I-7 in western Hancock County in the westernmost bulge of Illinois is of particular interest. In this area, the Maquoketa Shale Group, caprock for the Ottawa Limestone Megagroup-hosted ore deposits in the Upper Mississippi Valley Zinc-Lead District, and strata of Silurian age have been removed by pre-middle Devonian erosion. Carbonates of middle Devonian age rest directly on the Ottawa carbonates. Residue samples from a drill hole in the Maquoketa window contain more than 10,000 ppm (1%) zinc as sphalerite in the Devonian carbonate (about 100 ft thick) and lesser amounts (700 to 3,000 ppm) in the directly underlying Galena Group (appendix, I-7). The implication seems clear that metal-bearing fluids traversed Ottawa strata and were confined by the Maquoketa Shale Group cap until they encountered the Maquoketa window, ascended, and spread laterally into porous Devonian carbonates. Thick impermeable shales of late Devonian and early Mississippian age cap the Devonian carbonate. The Maquoketa window in Illinois may be compared to the upper Devonian and lower Mississippian Chattanooga Shale window beneath the Tri-State Zn-Pb District of Oklahoma, Missouri and Kansas.

Mississippian System. Figure 8 shows the location and total AMF content of insoluble residues of carbonate rocks of Mississippian

Figure 4 Ratio of zinc to zinc + lead + copper (in AMF) for insoluble residue samples from all geologic systems.

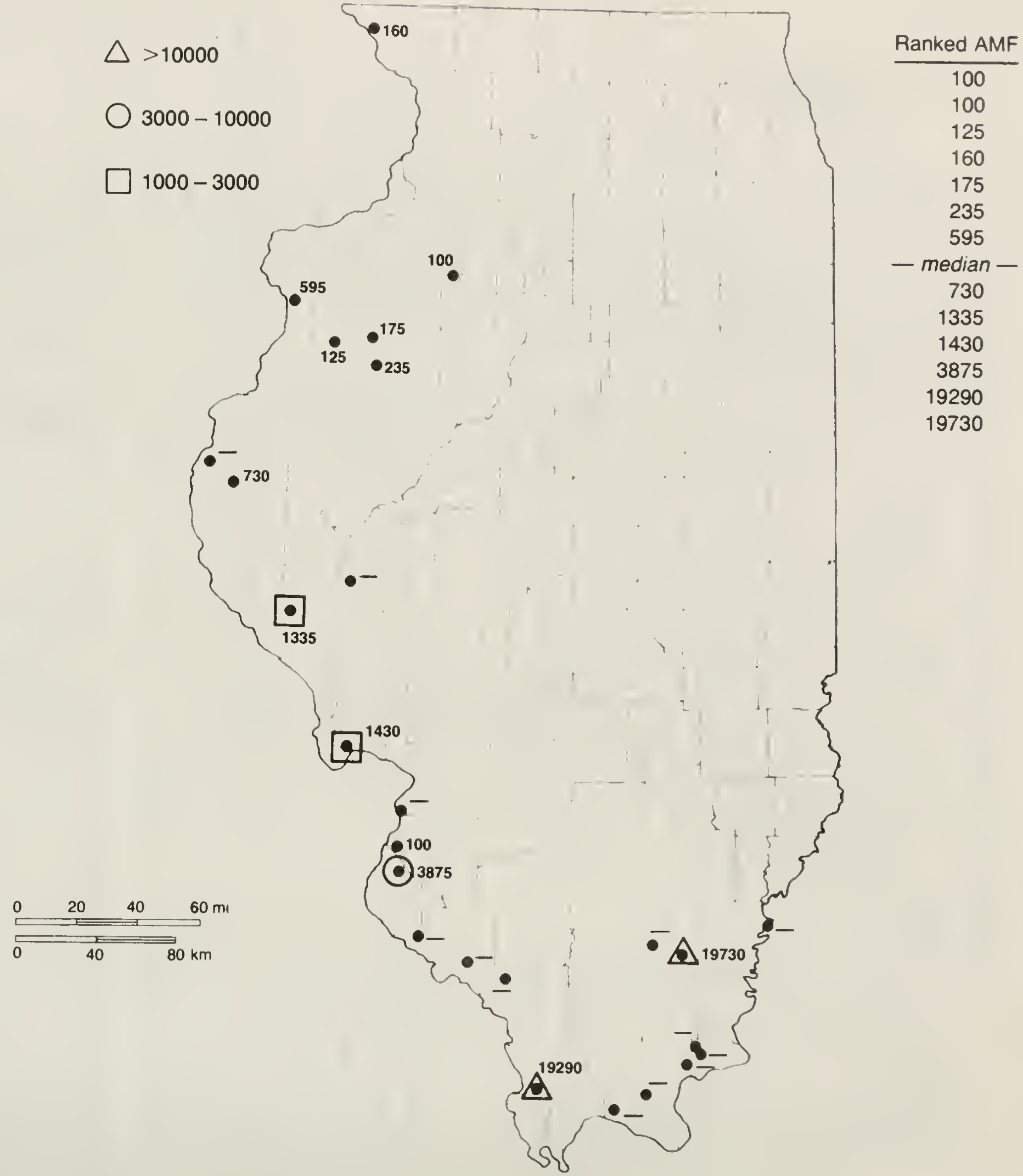
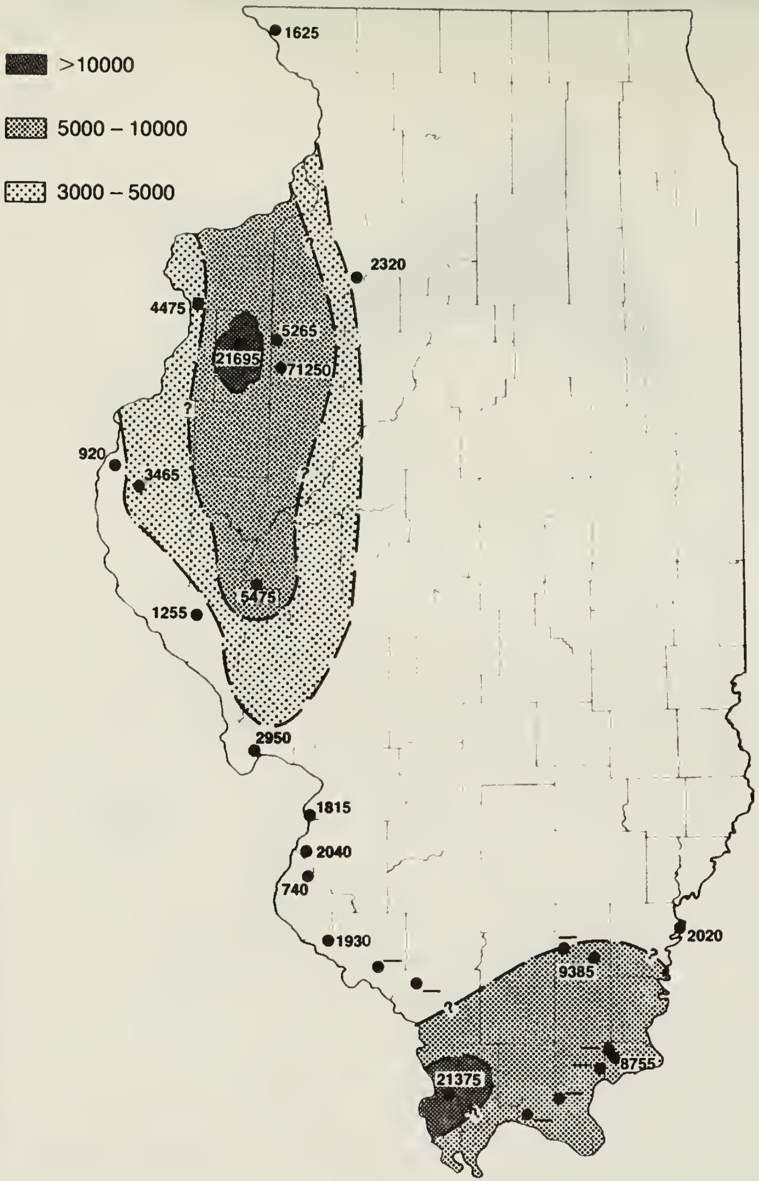
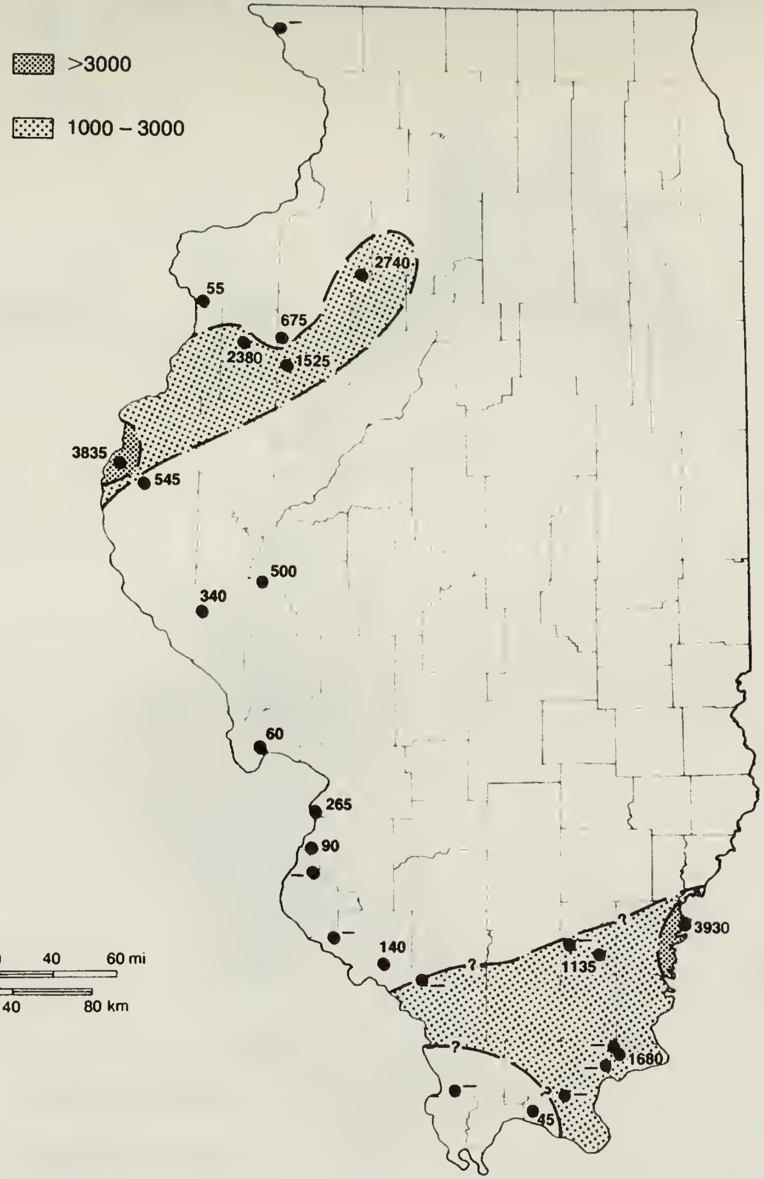


Figure 5 Total metal content (in AMF) of insoluble residue samples of Cambrian carbonate rocks; (—) indicates Cambrian not penetrated in drill hole.



Ranked AMF
740
920
1255
1625
1815
1930
2020
2040
2320
2950
— *median* —
3465
4475
5265
5475
7125
8755
9385
21375
21695

Figure 6 Total metal content (in AMF) of insoluble residue samples of Ordovician carbonate rocks; (—) indicates Ordovician not penetrated in drill hole.



Ranked AMF
45
55
60
90
140
265
340
500
545
— *median*
675
1135
1525
1680
2380
2740
3835
3930

Figure 7 Total metal content (in AMF) of insoluble residue samples of carbonate rocks of Silurian and/or Devonian age; (—) indicates Silurian-Devonian not penetrated in drill hole.

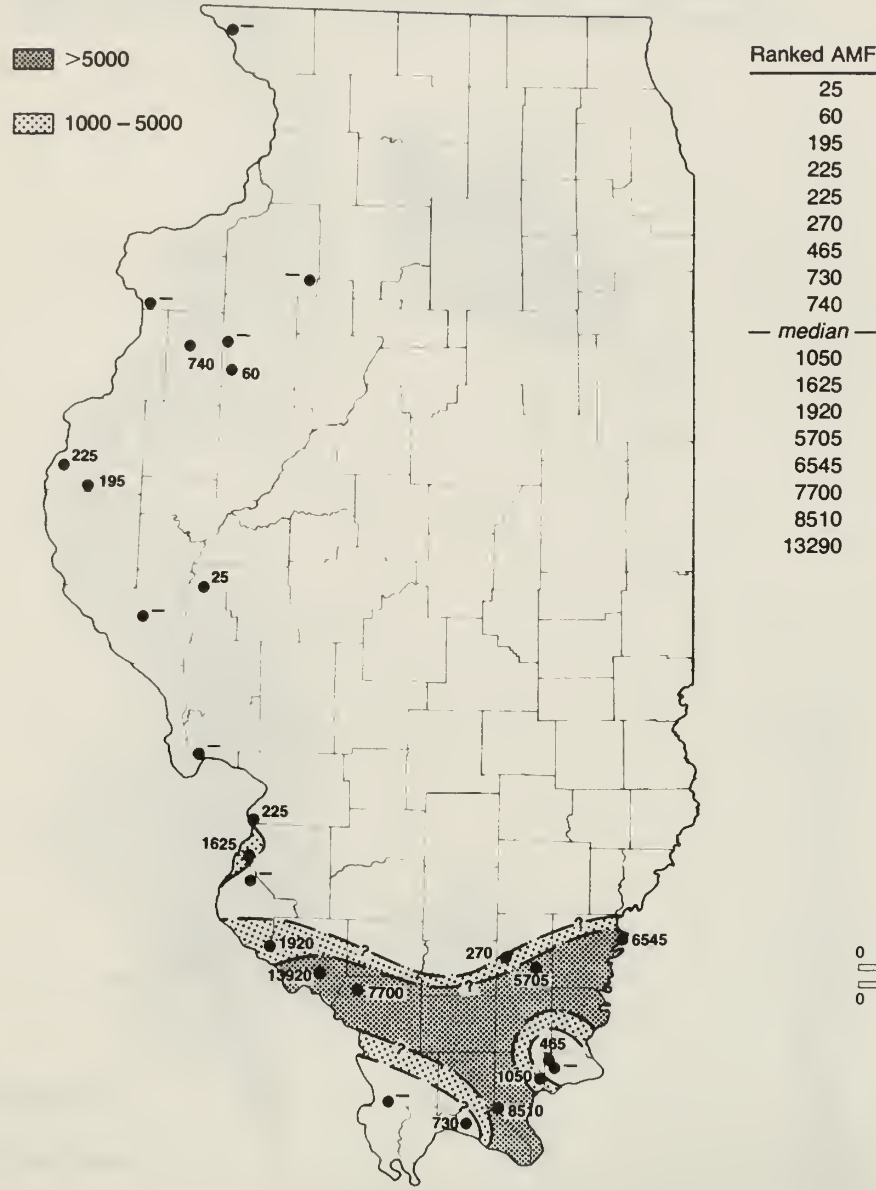


Figure 8 Total metal content (in AMF) of insoluble residue samples of Mississippian carbonate rocks; (—) indicates Mississippian not penetrated in drill hole.

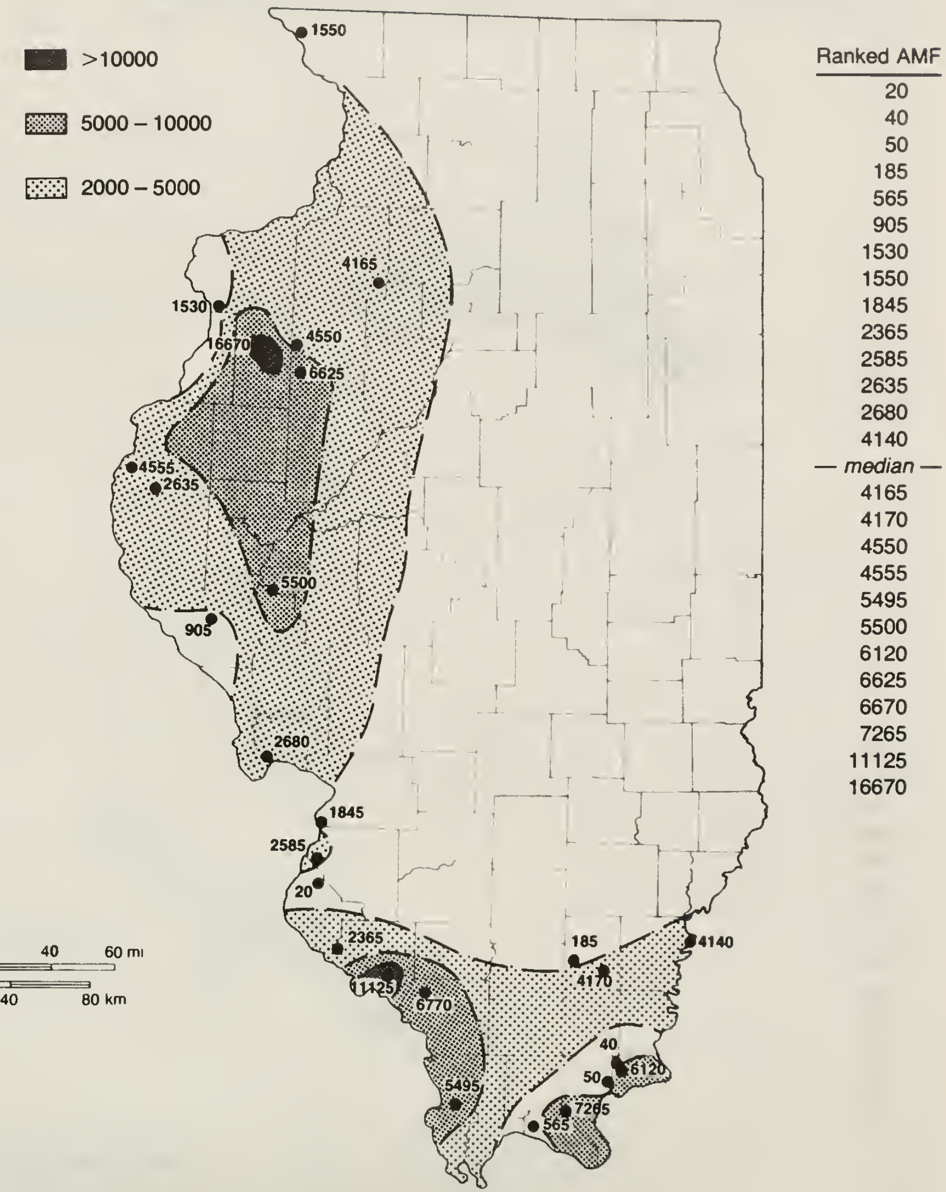


Figure 9 Zinc content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.

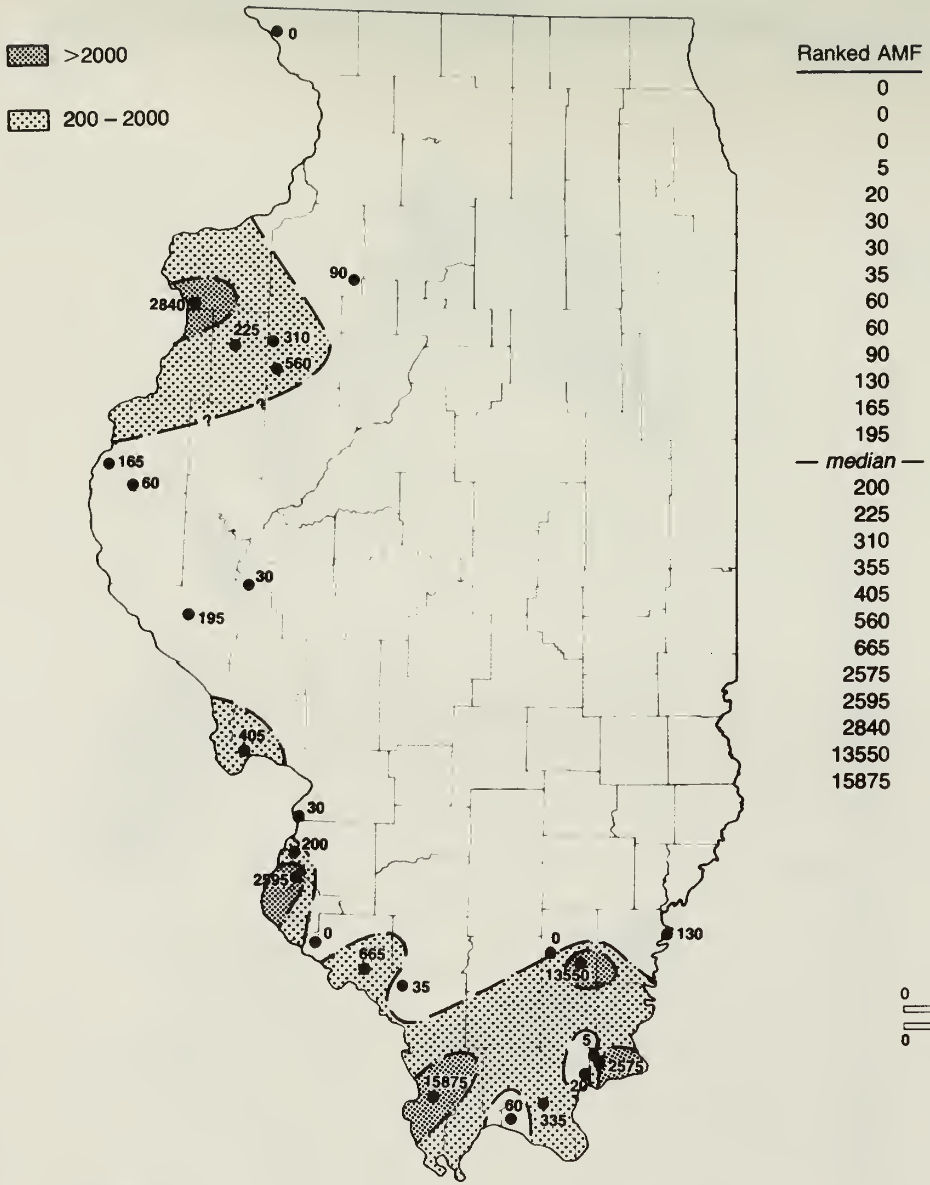


Figure 10 Lead content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.

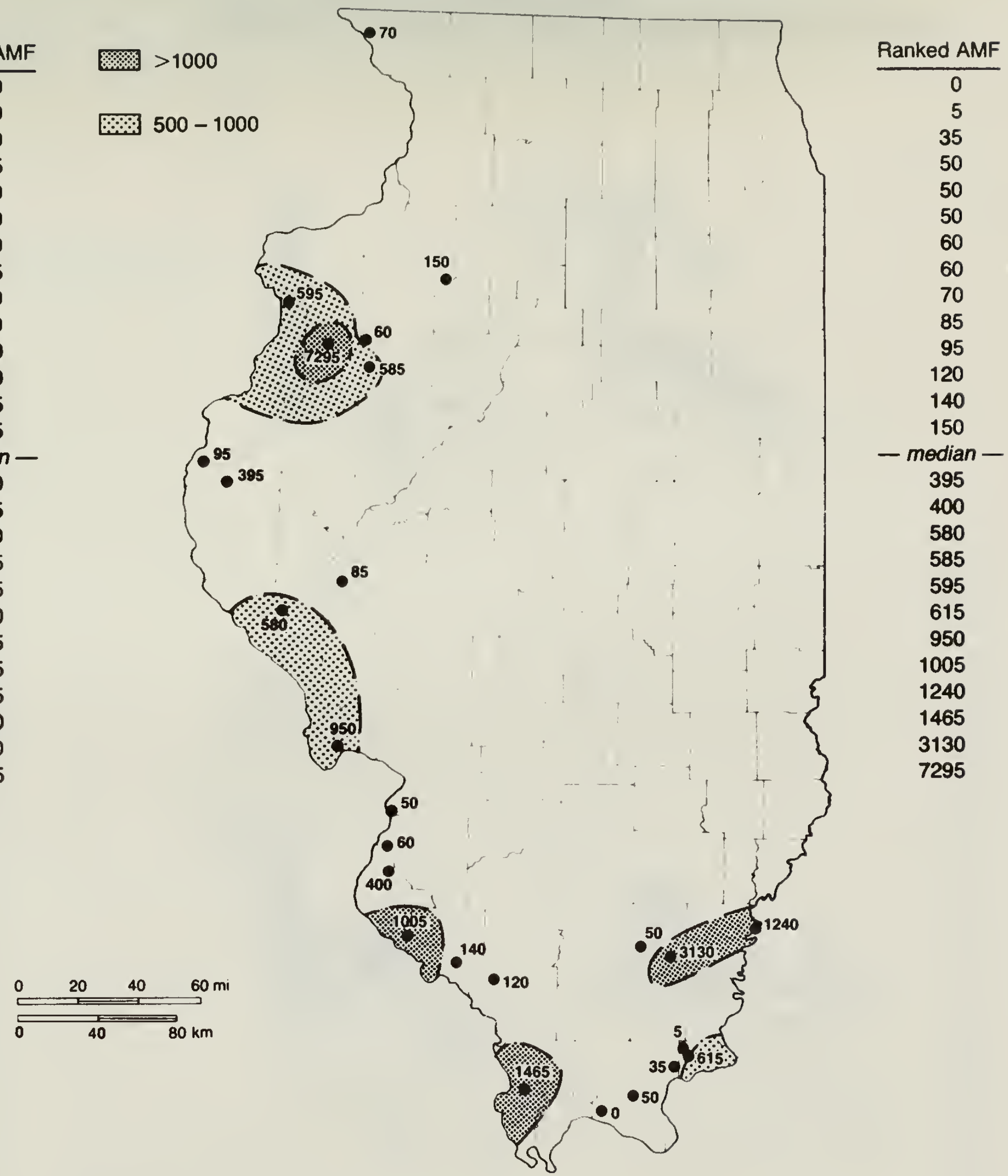
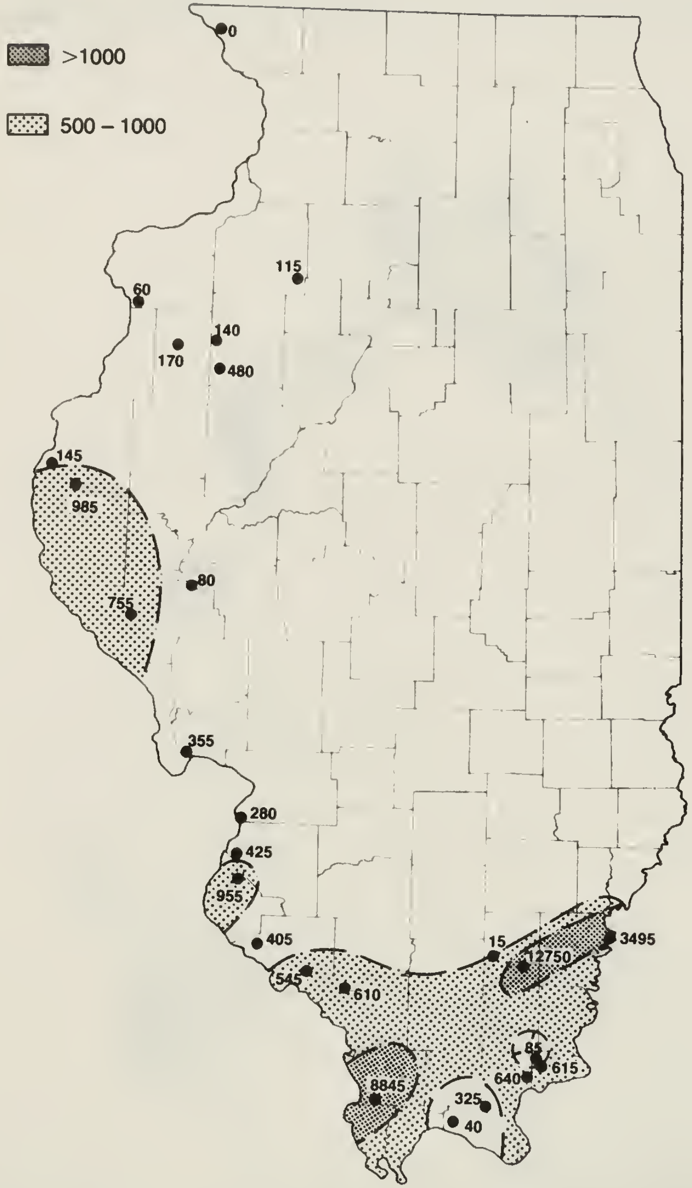
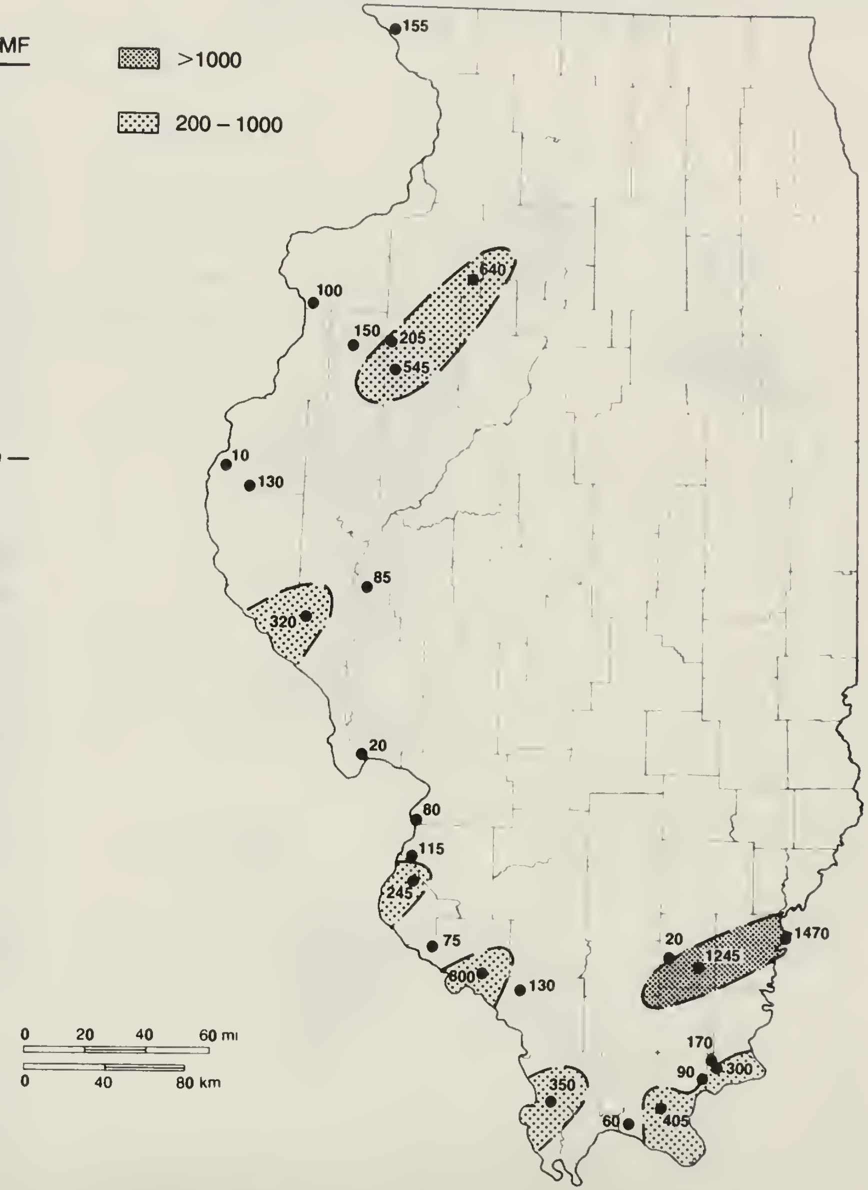


Figure 11 Copper content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.



Ranked AMF
0
15
40
60
80
85
115
140
145
170
280
355
375
405
— *median* —
425
480
545
610
615
640
755
955
985
3495
8845
12750



Ranked AMF
10
20
20
60
75
80
85
90
100
115
130
130
150
155
— *median* —
170
205
245
300
320
350
405
545
640
800
1245
1470

Figure 12 Molybdenum content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.

Figure 13 Nickel content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.

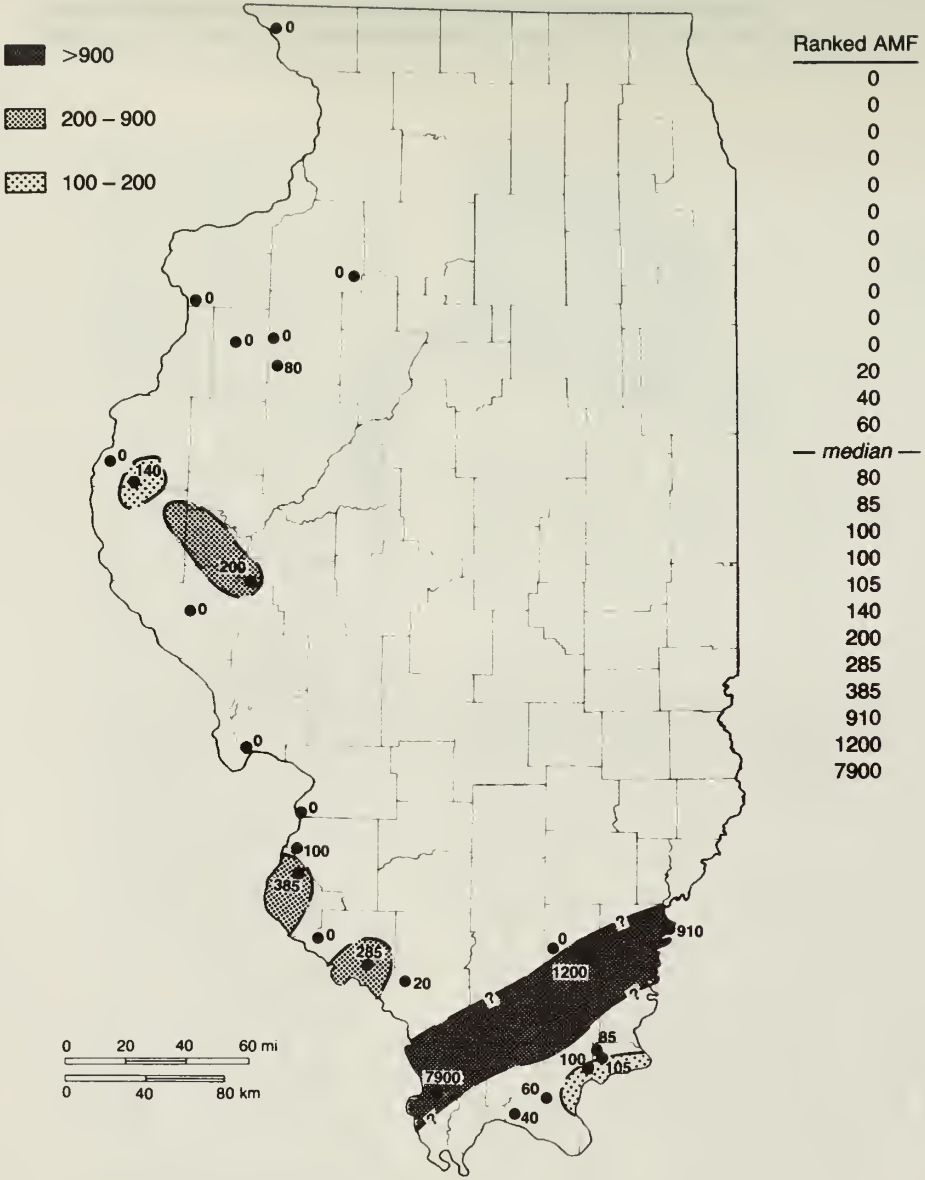


Figure 14 Silver content (in AMF) of insoluble residue samples of carbonate rocks from all geologic systems.

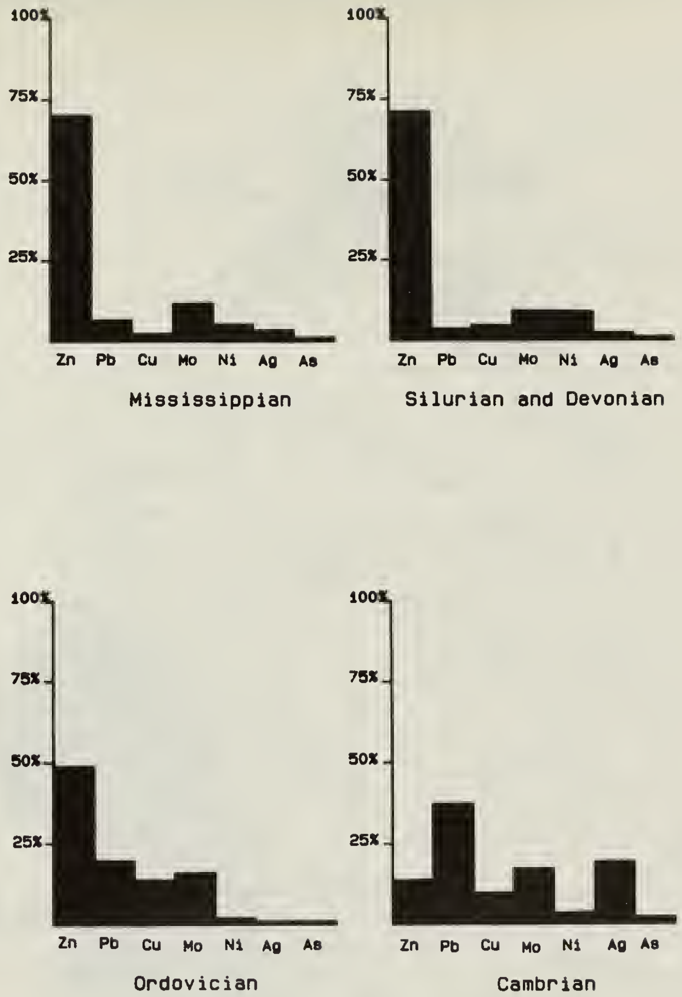


Figure 15 Contribution of each metal (%) to total AMF for each system.

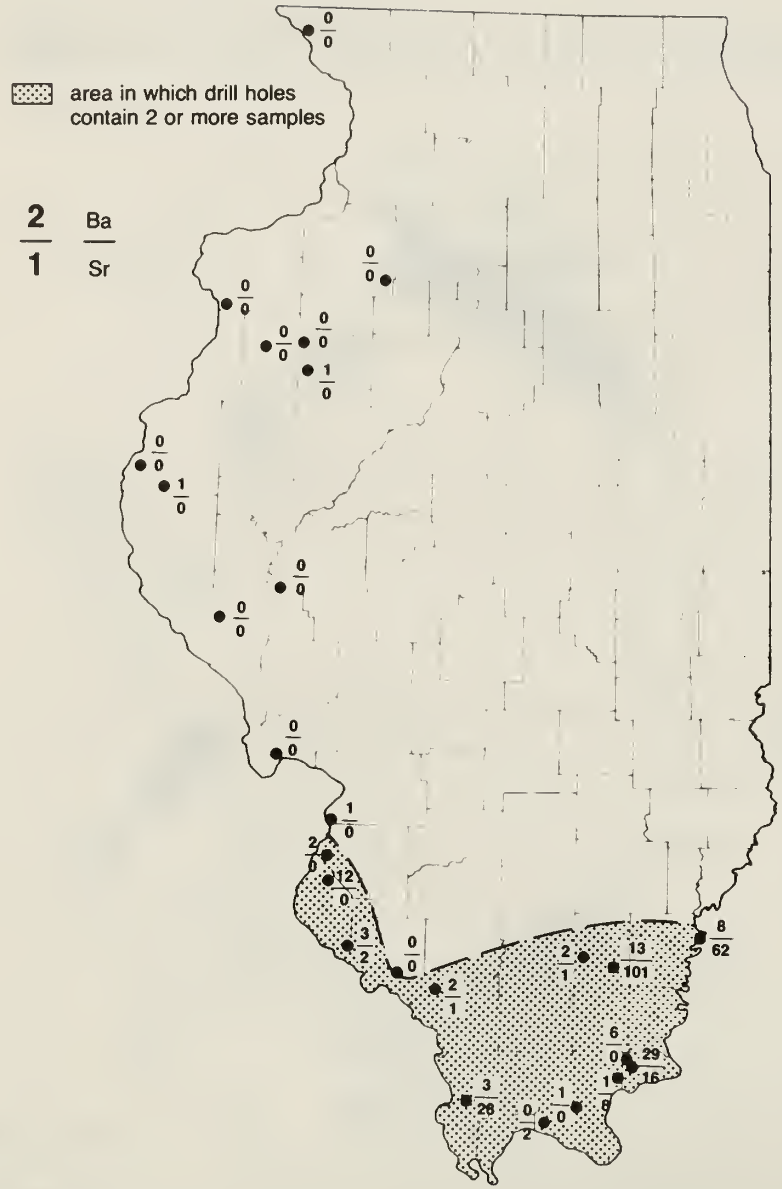


Figure 16 Number of insoluble residue samples in each drill hole that contain barium and/or strontium in concentrations of 5000 ppm or more.

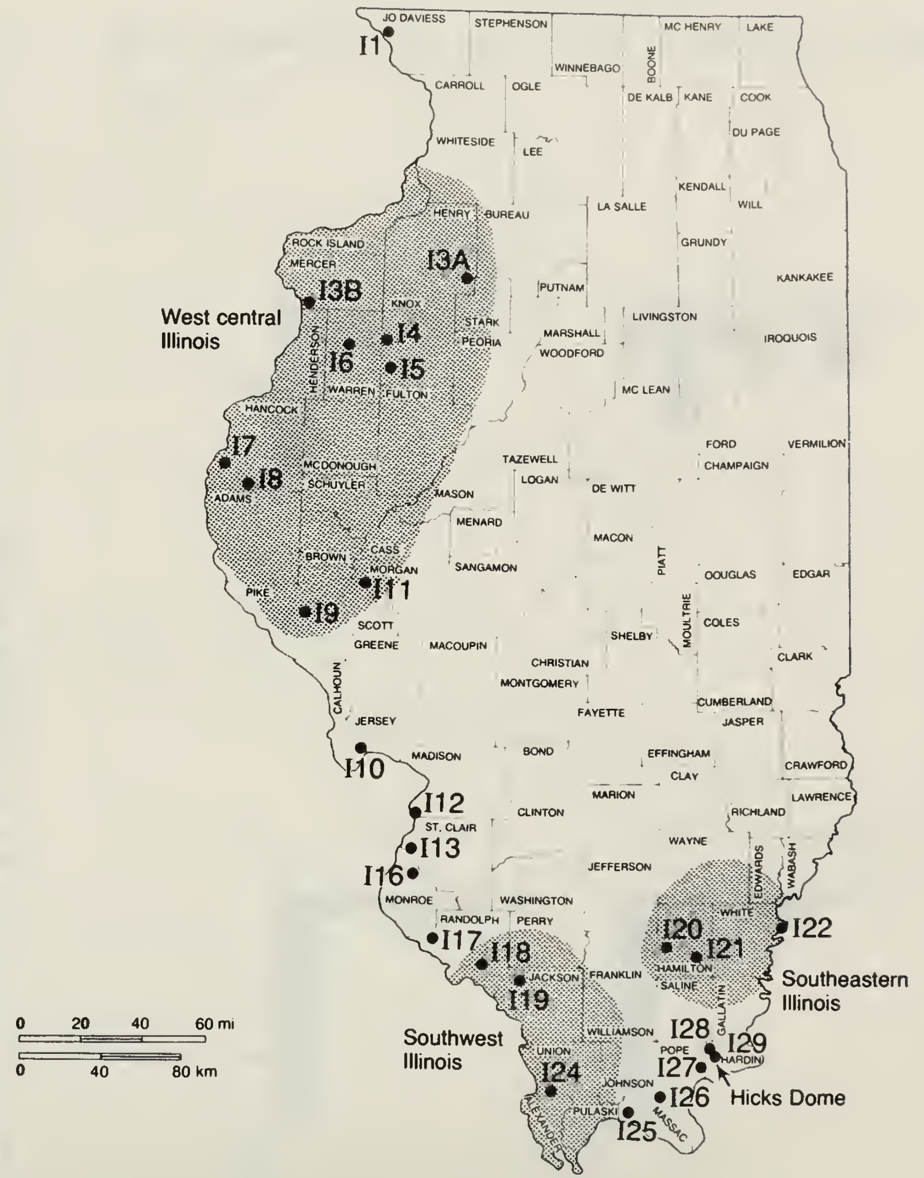


Figure 17 Map showing county locations of drill holes analyzed in study and regions that merit further study.

age. The concentration of high total AMF values in the Mississippian rocks of southern Illinois as compared to those in northern Illinois can be explained by the fact that there are no strata in northern Illinois correlative with the high-AMF Mississippian formations in southern Illinois. Seventeen drill holes in the study set penetrate Mississippian strata. Drill holes in southern Illinois penetrate thick limestone formation of the Mammoth Cave Limestone Megagroup--the Ullin and Salem of middle Valmeyeran age and the St. Louis and Ste. Genevieve of late Valmeyeran age. The Ste. Genevieve, St. Louis, and to a lesser extent, the upper part of the Salem, are hosts for replacement and/or vein type ore bodies in the Illinois-Kentucky Fluorspar District. The lower part of the St. Louis and upper part of the Salem contain high AMF values in southern Illinois. In drill holes to the north, the Mississippian system, where present, is represented mostly by Kinderhookian (lower Mississippian) shales and the overlying early Valmeyeran Burlington and Keokuk Limestones. From south to north, Mississipian formations are successively truncated--removed by post-Mississippian, pre-Pennsylvanian erosion. Analyses of selected samples from rocks of Pennsylvanian (undifferentiated) age were restricted to a single drill hole showing up to 300 ppm Zn in some residues (1-21, appendix).

Metal distribution by element

The geochemical maps showing the abundance (in AMF) of six individual metals (Zn, Pb, Cu, Mo, Ni, Ag) in each drill hole (figs. 9-14) indicate that metal-bearing fluids of variable composition have migrated through the subsurface rocks in southern and western Illinois. Anomalously high amounts of all of the six metals are present in southern Illinois, whereas zinc predominates in western Illinois. Barium and strontium are more abundant in southern Illinois than elsewhere; they occur in all the geologic systems sampled. Figure 16 shows the number of insoluble residue samples in each drill hole that contain 5000 ppm or more barium and 5000 ppm or more strontium. Strontium is not present in samples from the northern three-fourths of the drill hole transect. Barium is present in only one sample from each of two northern drill holes at the 5000 ppm concentration level. Strontium occurs in celestite and anhydrite, particularly in the deep part of the Illinois Basin (drill holes I-21 and I-22). Barium occurs in barite and is most abundant in the Fricker hole on the flank of Hicks Dome (I-29).

Ore deposit types suggested by study

The results of this study do not warrant our drawing conclusions about the extent of subsurface mineral potential of Illinois; that was not the objective of the study. Our findings do show regions of anomalously high subsurface metal values, permit speculation about possible regional target areas, and suggest specific concepts and models of mineral occurrence that should be further tested. The data suggest that at least four different types of ore deposit models should be considered in subsurface exploration in western and southern Illinois. Each model is based upon geologic and geochemical characteristics of a known mining district or mineral deposit. The specific models are:

- Ordovician-hosted and possible Devonian-hosted zinc-lead deposits in west-central and northwest Illinois similar to those in the Upper Mississippi Valley Zinc-Lead District;

- Mississippian-hosted fluorite, barite, zinc, lead deposits in southwestern Illinois similar to known deposits farther east in the Illinois-Kentucky Fluorspar District;

- Cambrian-hosted, lead-rich base metal deposits similar to those in the world-class Southeast Missouri Lead District;

- cryptovolcanic breccia-hosted deposits (Be, Nb, Y, REE, Th, Ba, F) similar to the known occurrence at Hicks Dome.

Attempts should be made to develop genetic ore deposit models in which the transport mechanism involves: (1) brines from the Illinois Basin that carried metal and sulfur from deep sedimentary metal sources, (2) hydrothermal processes and igneous sources related to Hicks Dome-type structures and rocks (subsilicic alkalic igneous rocks), and (3) combinations of (1) and (2) that involve mixing of sedimentary and igneous sources.

AREAS MERITING FURTHER ATTENTION

Southeastern Illinois

The pilot study includes analyses of residue samples from two oil tests in the deep part of the Illinois Basin (fig. 17) in southeastern Illinois, north of the Rough Creek Fault System. Drill hole I-21 in Hamilton County collars in rocks of Pennsylvanian age; it was sampled continuously to total depth in Precambrian granite at 13,051 feet. Drill hole I-22 in White County collars in Pennsylvanian rocks, is cored below 3050 feet to total depth, and bottoms in Canadian Series (lower Ordovician) rocks at 7683 feet. The core interval for I-22, which begins in carbonate rocks of Mississippian age (Valmeyeran Series), was sampled and analyzed. A short upper Valmeyeran section in a Hamilton County well was also analyzed (I-20).

The analytical results on residues from these holes have important implications for possible metal and sulfur sources and fluid migration. For the first time in the USGS midcontinent subsurface geochemical studies, trace element information has been obtained from deep basin stratigraphic units that host Mississippi Valley type (MVT) lead-zinc deposits on carbonate platforms between basins. The Illinois-Kentucky Fluorspar District is located near the center of the Illinois Basin, and in this setting is not a typical MVT deposit. The deep seated Hicks Dome breccia system and the fluorspar district fault system suggest a greater upward migration of fluid than that in MVT deposits located at the margins of basins. In addition to the high total AMF values of the deep basin holes (table 3), the occurrence of anhydrite and celestite in Ordovician and Mississippian carbonate rocks (Appendix I-21 and I-22) is of interest. The anhydrite occurs in thin beds and seams and contains 1 to 2 percent strontium. Celestite is secondary and occurs in fractures, joints, and vugs. In both holes, anhydrite is most abundant in the upper Salem and lower St. Louis Limestone succession of Mississippian age and the Ordovician Shakopee and Joachim Dolomites below and above the St. Peter Sandstone. There appears to be no correlation between anhydrite-celestite content and metal content. Small anomalous amounts of zinc are present in anhydrite zones in the Mississippian carbonates, but the anhydrite zones in Ordovician strata are not metal rich. The Cambrian section, penetrated only in drill hole I-21, is metal rich but does not contain anhydrite or celestite. These findings raise several questions:

- Are the sulfate minerals in the deep part of the Illinois Basin a possible sulfur source for MVT deposits?

- How will sulfur isotope data for anhydrite and celestite from the deep basin compare with sulfur isotope data for celestite associated with ore deposits in the Illinois-Kentucky Fluorspar District?

- Did the Rough Creek-Shawneetown Fault Zone that traverses the Illinois Basin from east to west provide a convenient channelway for migration of deep basin brines?

- Is the abundant and extensive suite of metals in the Cambrian carbonates deep in the basin (drill hole I-21) a potential source of metals for the MVT deposits?

The metal endowment, metal suite, and abundance of sulfate minerals in these two drill holes require further study and comparison with metal and sulfate analyses from all other deep drill holes in the basin. Informative patterns of distribution and abundance are certain to be revealed.

West-central Illinois

High AMF values, chiefly for zinc (figs. 6, 9), are present in residue samples from several drill holes in west-central Illinois (fig. 17). Most of the high values occur in carbonates of the Platteville and Galena Groups of Ordovician age. These units, part of the Ottawa Megagroup, host the zinc-lead deposits of the Upper Mississippi Valley (UMV) Zinc-Lead District in southwestern Wisconsin, northwestern Illinois, and eastern Iowa. These zinc occurrences suggest a southward extension of the UMV District. Middle Devonian carbonates in the Maquoketa window in Hancock County (discussed earlier) also have potential for zinc deposits. Fluid flow in this broad area, confined to the porous Platteville and Galena carbonates, would seek to escape through the Maquoketa window. Tremendous volumes of metal-bearing fluids may have been funneled upward through this passage.

The similarity of the Maquoketa window in Hancock County to the geologic setting in the world-class Tri-State Zinc District of Oklahoma, Kansas, and Missouri is striking. The Chattanooga Shale window in the Tri-State is thought to have provided fluid access from Cambrian and Ordovician strata into the overlying Mississippian carbonate host rocks, which are capped by thick Pennsylvanian shale. The Maquoketa Shale window in Illinois may have played the same role--i.e., concentrating and funneling metal-bearing fluids from carbonates of the Ottawa Megagroup (the ore hosts in the UMV district to the north) into a relatively thin middle Devonian carbonate--within which they could be trapped under thick late Devonian or Mississippian shale cover.

Although the pilot study data points are sparse, findings suggest that the Devonian carbonates and the Platteville through Galena interval would seem to be favorable prospecting ground in this part of Illinois. Depth to Devonian in this area is about 600 feet.

Southwest Illinois

Drill hole I-24, a deep oil test in Union County in southwest Illinois (fig. 17), was drilled on the upthrown side of a faulted structural high (Bristol and Buschbach, 1973); it was collared in the Maquoketa Shale Group and bottoms in the Mt. Simon ("Lamotte") Sandstone of Cambrian age at a depth of 8492 feet. When analytical results from this hole (appendix I-24) are compared with those from other drill holes in southern Illinois, they reveal several unusual aspects about the high AMF values in carbonates of Cambrian, Ordovician, and Mississippian age (figs. 5, 6, and 8). Analysis of most drill holes in southern Illinois show small but anomalous amounts of molybdenum throughout the Paleozoic section. High AMF values, particularly Pb, Cu, and Mo occur in Canadian (lower Ordovician) carbonates. Strontium, as celestite, is abundant (more than 5000 ppm) in the upper part of the Canadian section. High zinc-rich metal values occur in Ottawa Megagroup carbonates (Platteville and Galena Groups), and the Canadian is essentially barren with respect to zinc. In I-24, the Ottawa contains only erratic shows of zinc and lead, but strontium, as celestite, is abundant in the residues in the interval 920 to 1300 feet and is a major component of the residue from 1065 to 1150 feet. Unusually high amounts of Ag occur in Cambrian carbonates in the interval from 6840 to 7080 feet. Hand-picked, coarsely crystalline pyrite from this interval contained 100 ppm Ag as well as 1500 ppm Pb, 1000 ppm As, and 1000 ppm Zn. Another unusual aspect is the abundance of zinc, as sphalerite, in dolomite of the Eau Claire Formation (the stratigraphic equivalent to the Bonneterre Formation of the Missouri Lead Belt), and deep in the Cambrian section.

These analyses and the analyses of drill holes I-21 and I-22 in the central part of the Illinois Basin discussed previously indicate that the Illinois Basin should be considered a possible source area for MVT deposits.

Hicks Dome

Hicks Dome in Hardin County in the northern part of the Illinois-Kentucky Fluorspar District (fig. 17) is a striking structural feature that has been described by Brown et al. (1954) as an incipient cryptovolcanic structure. This interpretation is based in part upon an oil test, known as the Hamp hole, drilled at the apex of the dome by St. Joseph Lead Company in 1952. Brown et al. noted that

> a normal sequence of formations was encountered down to 1600 feet, but at about that depth the drill entered a confused brecciated zone, which persisted to the bottom of the hole at 2944 feet. This is interpreted as one of the explosion-type breccias, or diatremes, common in this Illinois-Kentucky area, as well as in nearby Missouri....the brecciated portion of the hole was mineralized continuously but erratically with fluorspar generally ranging from about 5 percent in the upper portion of the breccia to 2 percent at the bottom. This is much deeper than previously known in such amounts in the area.

Heyl and Brock (1961), in a discussion of the regional structural framework of the Illinois-Kentucky Fluorspar District, reported that the dome contains mineralized explosion breccias and altered periodotite dikes and is surrounded by arcuate and radial faults. They also reported that the breccia from the Hamp hole contained, in addition to fluorite, "much barite, quartz, calcite, and a little pyrite, sphalerite, galena, biotite, and apatite. Thorium, rare earths, beryllium, zirconium, and niobium are intimately associated with the fluorite and barite and increase in amount with these minerals."

Trace (1960) reported the occurrence of monazite, a cerium phosphate, and florencite, a cerium-aluminum phosphate, in a surface breccia sample. Trace's monazite was later identified as brockite (Heyl, personal communication, 1987). Baxter and Bradbury (1981) identified bertrandite, a hydrous beryllium silicate in cuttings from the Hamp hole and from a mineralized (fluorite) shale breccia dike at the surface.

Heyl and Brock (1961) suggested that a genetic relationship exists between the Hicks Dome cryptovolcanic structure and the rest of the fluorspar district. The geology of the area has been mapped in detail by Baxter and Desborough (1965) and Baxter, Desborough, and Shaw (1967). Their maps demonstrate the structural complexity of the area and show the location of intrusive breccias and igneous dikes. The petrology and petrography of the dikes, sills, and breccias of southeastern Illinois, including "explosion" breccias at

Hicks Dome, have been described by Clegg and Bradbury (1956). Little new information is currently available, but publication of studies on the petrography and chemistry of Hicks Dome intrusive breccias (Bradbury and Baxter, in preparation) and on the unusual, if not unique, suite of minerals at Hicks Dome (Heyl et al., in preparation) should help unravel the origin and geologic history of this enigmatic structure.

For this pilot study, insoluble residue samples from the Fricker well, an oil test drilled in 1935 on the southeast flank of Hicks Dome about 3/4 mile southeast of the 1952 Hamp hole, were split from the sample library of the Illinois State Geological Survey and analyzed. According to the ISGS log, the Fricker well collars in the New Albany Shale of late Devonian and early Mississippian age and bottoms at 3306 feet in the Dutchtown Limestone (middle Ordovician), probably just above the St. Peter Sandstone. However, white quartz sand is common in the residues below 3120 feet.

Most of the residue samples beginning just below the Maquoketa Shale Group at about 2100 feet and continuing to the bottom of the hole (about 1200 feet of section) are a very fine, dark gray to black silty powder suggestive of black jasperiod. Traces of purple fluorite and pyrite are common. Spectrographic analyses of this material (appendix, 1-29) revealed the same unusual suite of elements that is present in the breccia from the Hamp hole and, prior to the present study, thought to be restricted to the immediate Hicks Dome area. Although enhanced element concentrations are to be expected in insoluble residue samples, some elements are concentrated in exceptionally high amounts. Beryllium is particularly abundant--more than 1000 ppm throughout much of the jasperoid(?) section. The Be standard was 1000 ppm for spectrographic comparison. Barium is consistently present in amounts greater than 5000 ppm. Niobium is present in amounts up to 2000 ppm near the top of this interval where titanium occurs in amounts greater than 1 percent. This spatial correlation suggests that the Nb occurs in titanium minerals such as rutile, brookite, or perovskite. Yttrium, thorium, and strontium, as well as zinc and lead, are particuarly abundant in the interval 2700 to 3100 feet. Although very little sample material is available from this well, more rigorous mineralogic and analytical techniques should be applied to this material to determine mineralogy and element abundances. It is intriguing to note that the mineralized interval in this well--about 1100 feet--is the same as that reported for the Hamp hole by Brown and others (1954) 3/4 mile away.

Trace amounts of the Hicks Dome chemical suite, particuarly of niobium, are present in drill hole I-27, a shallow Mississippian oil test a few miles southwest of Hicks Dome, and in I-28, a fluorspar test northwest of Hicks Dome.

CONCLUSIONS

All participants in this pilot study agree that the study results (1) demonstrate the feasibility of using insoluble residues of carbonate rocks as a sample medium for geochemical exploration in Illinois; (2) reveal anomalously high subsurface metal values suggesting areas in western and southern Illinois that merit further investigation; and (3) have important genetic implications that suggest new avenues of research on ore-forming processes and metal and sulfur sources in the Illinois Basin.

REFERENCES

Baxter, J. W., and J.C. Bradbury, 1981, Bertrandite at Hicks Dome, Hardin County, Illinois: Illinois State Academy of Science Transactions, v. 73, no. 1, p. 1-11.

Baxter, J. W., and G. A. Desborough, 1965, Areal geology of the Illinois Fluorspar District. Part 2: Karbers Ridge and Rosiclare Quadrangles: Illinois State Geological Survey Circular 385, 40 p.

Baxter, J. W., G. A. Desborough, and C. W. Shaw, 1967, Areal geology of the Illinois Fluorspar District. Part 3: Herod and Shetlerville Quadrangles: Illinois State Geological Survey Circular 413, 41 p.

Bradbury, J. C. and J. W. Baxter, 1987, Intrusive breccias at Hicks Dome, Hardin County, Illinois: Illinois State Geological Survey, in preparation.

Bristol, H. M., and T. C. Buschbach, 1973, Ordovician Galena Group (Trenton) of Illinois--Structure and oil fields: Illinois State Geological Survey Illinois Petroleum 99, 38 p.

Brown, J. S., J. A. Emery, and P. A. Meyer, Jr., 1954, Explosion pipe in test well on Hicks Dome, Hardin County, Illinois: Economic Geology, v. 49, no. 8, p. 891-902.

Clegg, K. E., and J. C. Bradbury, 1956, Igneous intrusive rocks in Illinois and their economic significance: Illinois State Geological Survey Report of Investigations 197, 19 p.

Erickson, R. L., E. L. Mosier, and J. G. Viets, 1978, Generalized geologic and summary geochemical maps of the Rolla 1° x 2° quadrangle, Missouri: U.S. Geological Survey Miscellaneous Field Studies Map MF-1004-A.

Erickson, R. L., E. L. Mosier, J. G. Viets, and S. C King, 1979, Generalized geologic and geochemical maps of the Cambrian Bonneterre Formation, Rolla 1° x 2° quadrangle, Missouri: U.S. Geological Survey Miscellaneous Field Studies Map MF-1004-B.

Erickson, R. L., M. S. Erickson, E. L. Mosier, and Barbara Chazin, 1985, Summary geochemical and generalized geologic maps of the Springfield 1° x 2° quadrangle and adjacent area, Missouri: U.S. Geological Survey Miscellaneous Field Studies Map MF-1830-A.

Grimes, D. J., and A. P. Marranzino, 1968, Direct-current arc and alternating-current spark emission spectrographic field methods for semiquantitative analyses of geologic materials: U.S. Geological Survey Circular 591, 6 p.

Heyl, A. V., Jr., and M. A. Brock, 1961, Structural framework of the Illinois Kentucky mining district and its relation to mineral deposits, in Short papers in the geologic and hydrologic sciences: U.S. Geological Survey Professional Paper 424-D, p. D3-D6.

Heyl, A. V., Jr., 1972, The 38th parallel lineament and its relationship to ore deposits: Economic Geology, v. 67, p. 880.

Heyl, A. V., J. W. Adams, G. A. Desborough, J. L. Jolly, and R. D. Trace, Mineralogy and structure of the fluorine, barium, thorium, REE, niobium, beryllium, titanium deposits of the Hicks Dome Cryptovolcano, Illinois-Kentucky Mineral District U.S.A.: British Institution of Mining and Metallurgy, Applied Earth Science Transactions Section B, in preparation.

Martin, J. A., and W. P. Pratt, 1985, Geology and mineral-resource potential of the Springfield 1° x 2° quadrangle, Missouri, as appraised in September 1985: Missouri Department of Natural Resources, Division of Geology and Land Survey Open-File Report OFR-85-42-MR.

Pratt, W. P. [ed.], 1981, Metallic mineral resource potential of the Rolla 1° x 2° quadrangle, Missouri, as appraised in September 1980: U.S. Geological Survey Open-File Report 81-518, 77 p.

Schwalb, H. R., 1982, Paleozoic geology of the New Madrid area: Illinois State Geological Survey for U.S. Nuclear Regulatory Commission, NUREG/CR-2909, 61 p.

Trace, R. D., 1960, Significance of unusual mineral occurrence at Hicks Dome, Hardin County, Illinois, in Short papers in the geological sciences: U.S. Geological Survey Professional Paper 400-B, B63-B64.

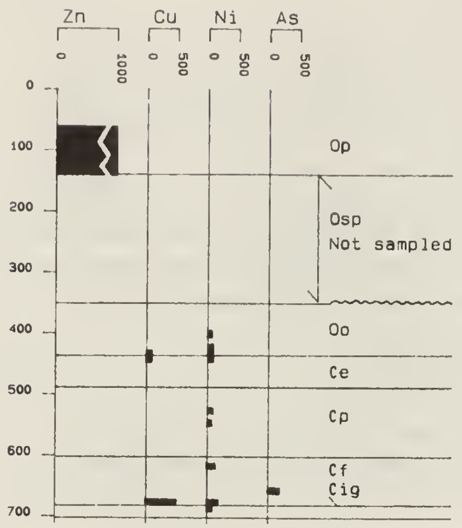
Willman, H. B., E. Atherton, T. C. Buschbach, C. Collinson, J. C. Frye, M. E. Hopkins, J. E. Lineback, and J. A. Simon, 1975, Handbook of Illinois Stratigraphy: Illinois State Geological Survey Bulletin 95, 261 p.

APPENDIX--GEOCHEMICAL LOGS OF DRILL HOLES

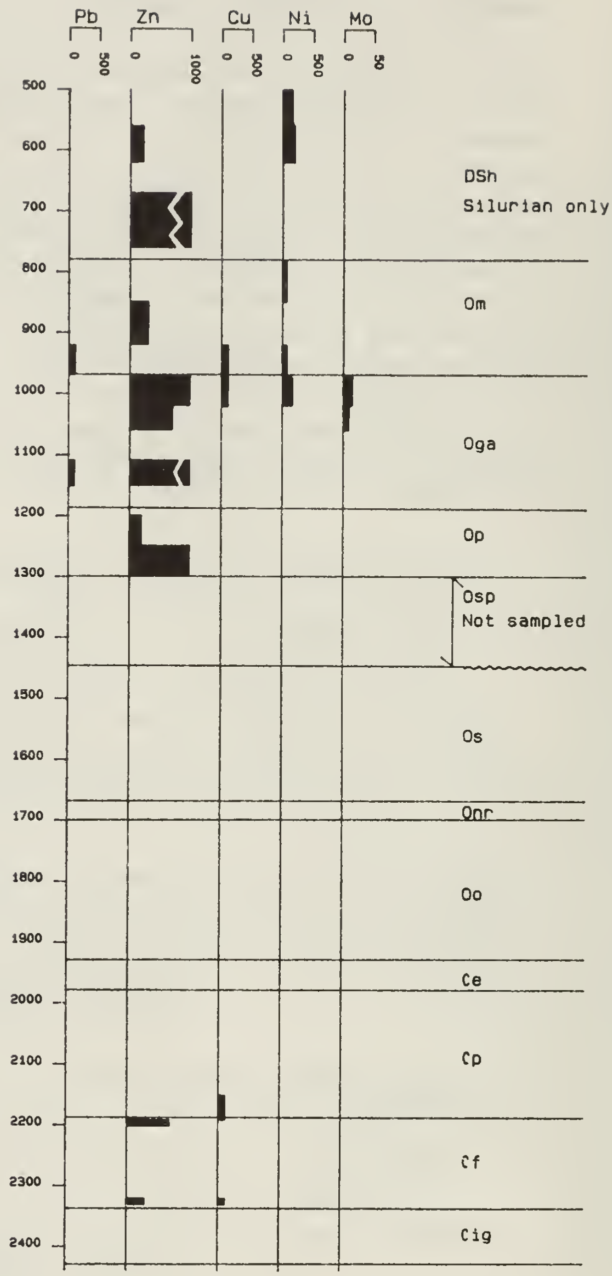
The stratigraphic distributions of anomalous contents of selected metals (in parts per million) in insoluble residue samples of carbonate rocks from each drill hole analyzed in this study are shown in the following bar graphs. These bar graphs enable the user to refer to a specific drill hole shown on the geochemical maps to determine stratigraphic position, metal suite and relative abundance of each metal, and intensity, continuity, thickness, and depth from surface of geochemically anomalous zones. Metal contents less than the minimum anomalous contents are not graphed. (See text for listing of minimum anomalous metal contents.)

The stratigraphic names and boundaries used on the bar graphs are standard Illinois State Geological Survey nomenclature (Willman et al., 1975). The following stratigraphic abbreviations are used:

Pennsylvanian:	Pu	Undifferentiated
Mississippian:	Muc	Grove Church Shale through Tar Springs Sandstone
	Mmc	Glen Dean Limestone through Beech Creek Limestone
	Mlc	Cypress Sandstone through Shetlerville Limestone
	Muv	Levias Limestone through St. Louis Limestone
	Mlv	Salem Limestone to base of Valmeyeran
	Mknh	North Hill Group
	Mkc	Chouteau Limestone
Mississippian and Devonian:	MDna	New Albany Shale Group
Devonian and Silurian:	DSh	Hunton Limestone Megagroup
Ordovician:	Om	Maquoketa Shale Group
	Oga	Galena Group
	Op	Platteville Group
	Oj	Joachim Dolomite
	Od	Dutchtown Limestone
	Osp	St. Peter Sandstone
	Oe	Everton Dolomite
	Os	Shakopee Dolomite
	Onr	New Richmond Sandstone
	Oo	Oneota Dolomite
Cambrian:	Ce	Eminence Formation
	Cp	Potosi Dolomite
	Cf	Franconia Formation
	Cig	Iron-Galesville Sandstones
	Cec	Eau Claire Formation
	Cms	Mt. Simon Sandstone
Precambrian:	pC	Precambrian Basement



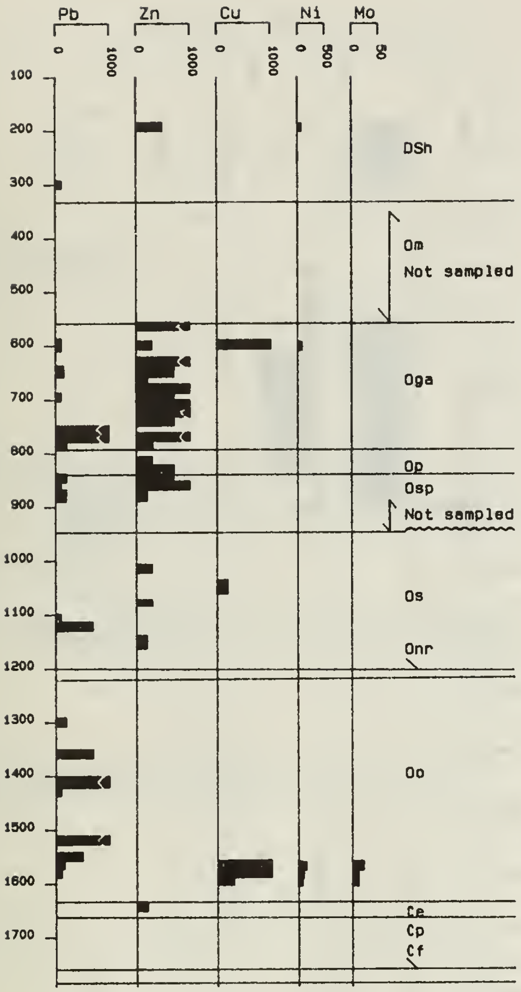
I-1: total depth 1513 feet. Clastics from 700 to 1513 were not sampled.



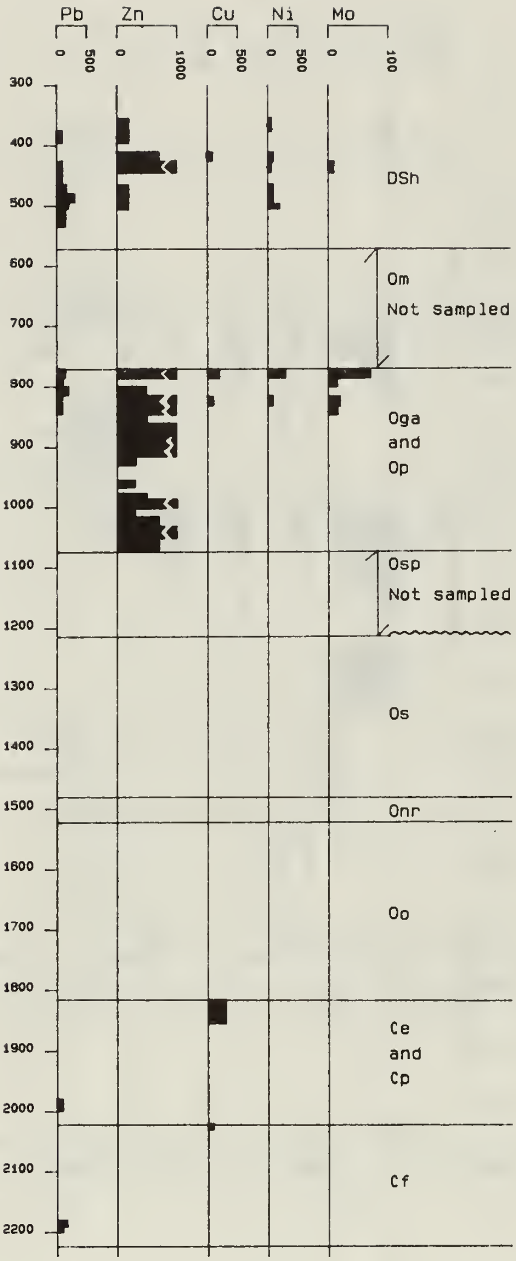
I-3A: total depth 2430 feet.

Abbreviations for elements discussed in pilot study

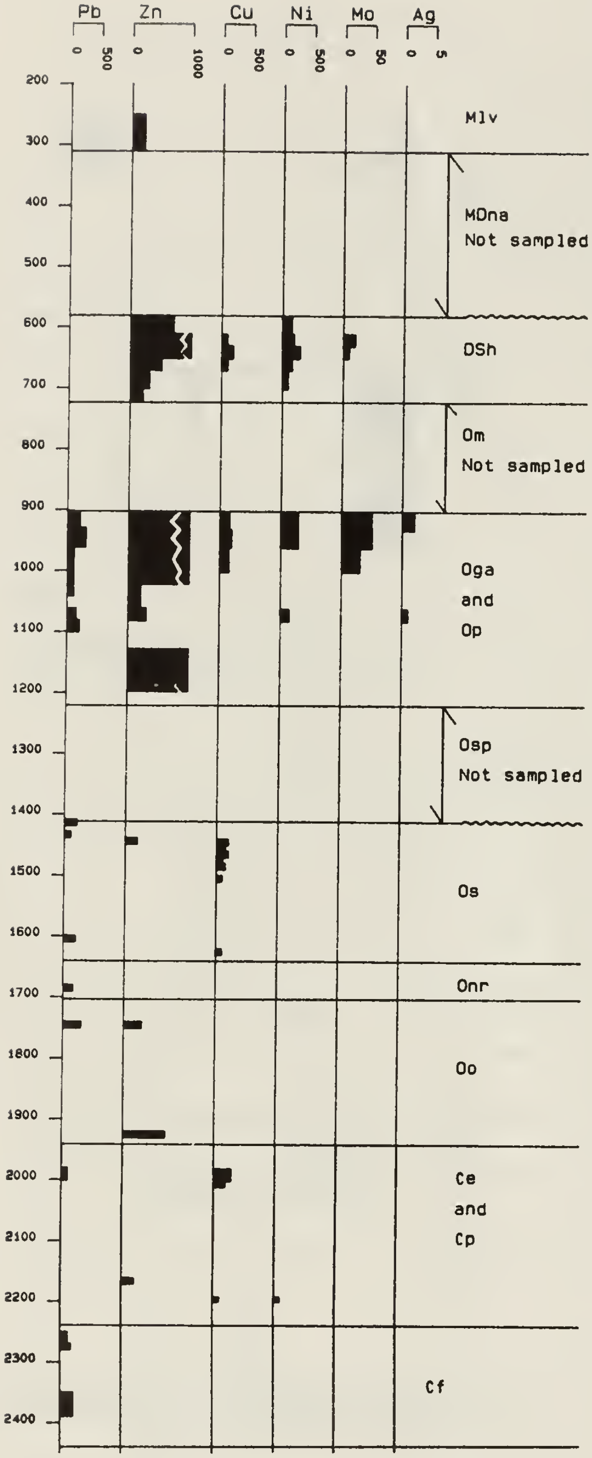
Ag	Silver
As	Arsenic
Ba	Barium
Be	Beryllium
Cu	Copper
Mo	Molybdenum
Nb	Niobium
Pb	Lead
Sr	Strontium
Th	Thorium
Y	Yttrium
REE	Rare earth elements
Zn	Zinc



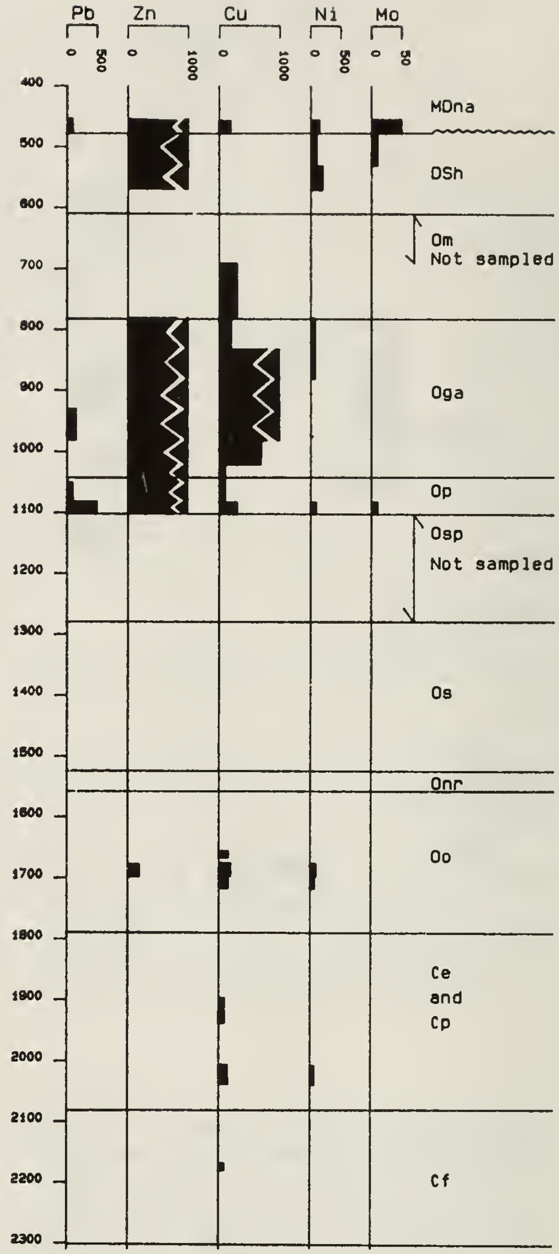
I-3B: total depth 3706 feet; missing sample interval 1780 to 2965 feet. Mt. Simon sandstone was analyzed from 2965 to 3205 feet but is not shown on the bar graph (no anomalous metal values were detected). Granite wash from 3250 to 3706 feet. Two samples of granite wash in the 3250 to 3275 feet interval were analyzed; lead content was 100 and 150 ppm.



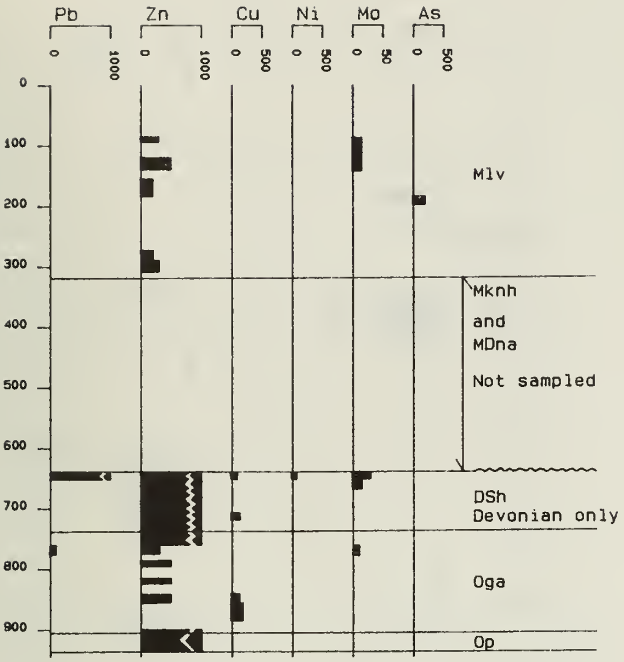
I-4: total depth 2407 feet. Clastics from 2220 to 2407 feet were not sampled.



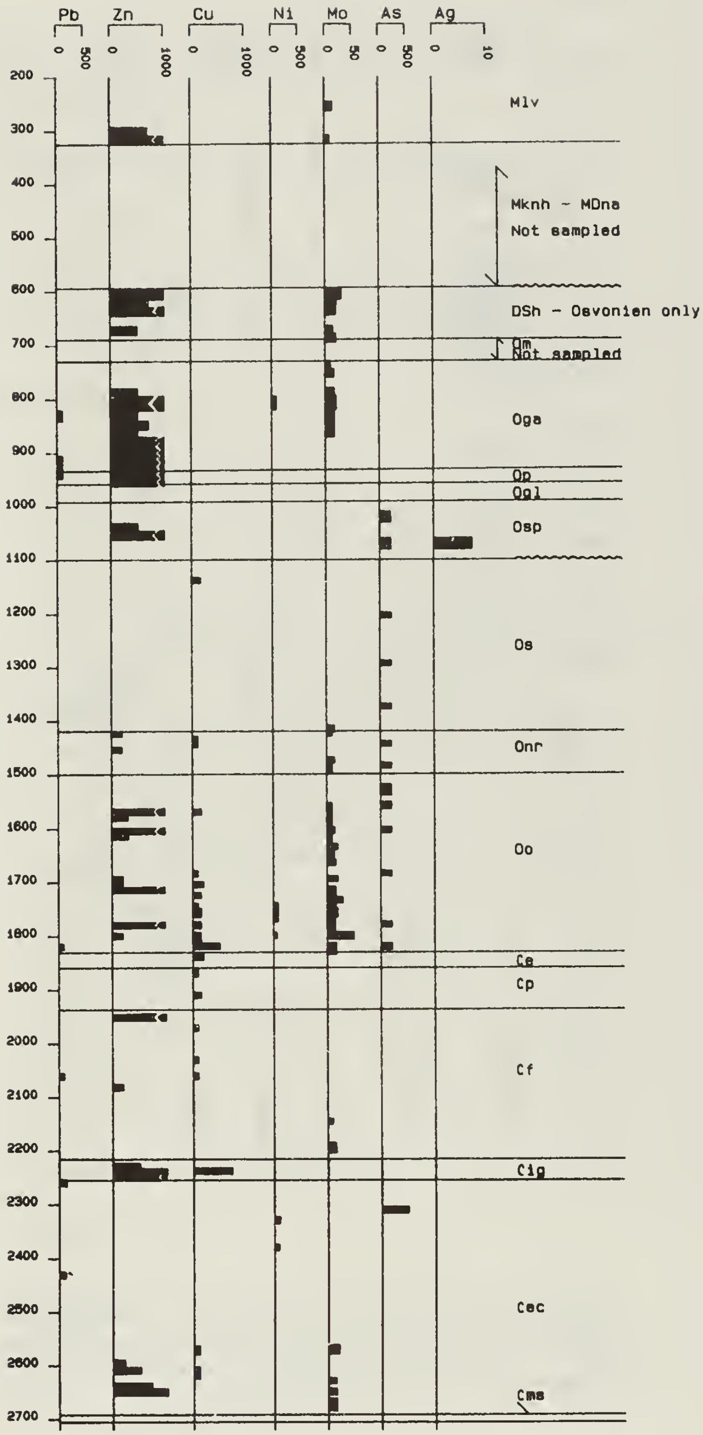
I-5: total depth 2588 feet. Clastics from 2440 to 2588 feet were not sampled.



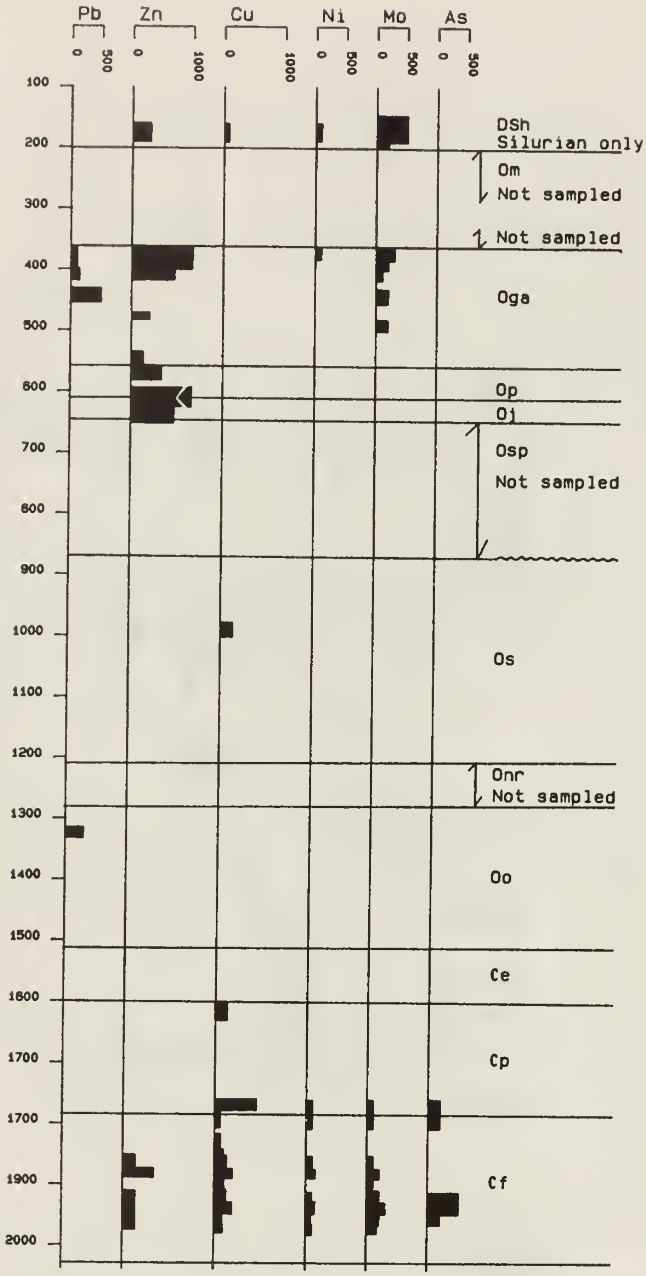
I-6: total depth 2445 feet. Clastics from 2300 to 2445 feet were not sampled.



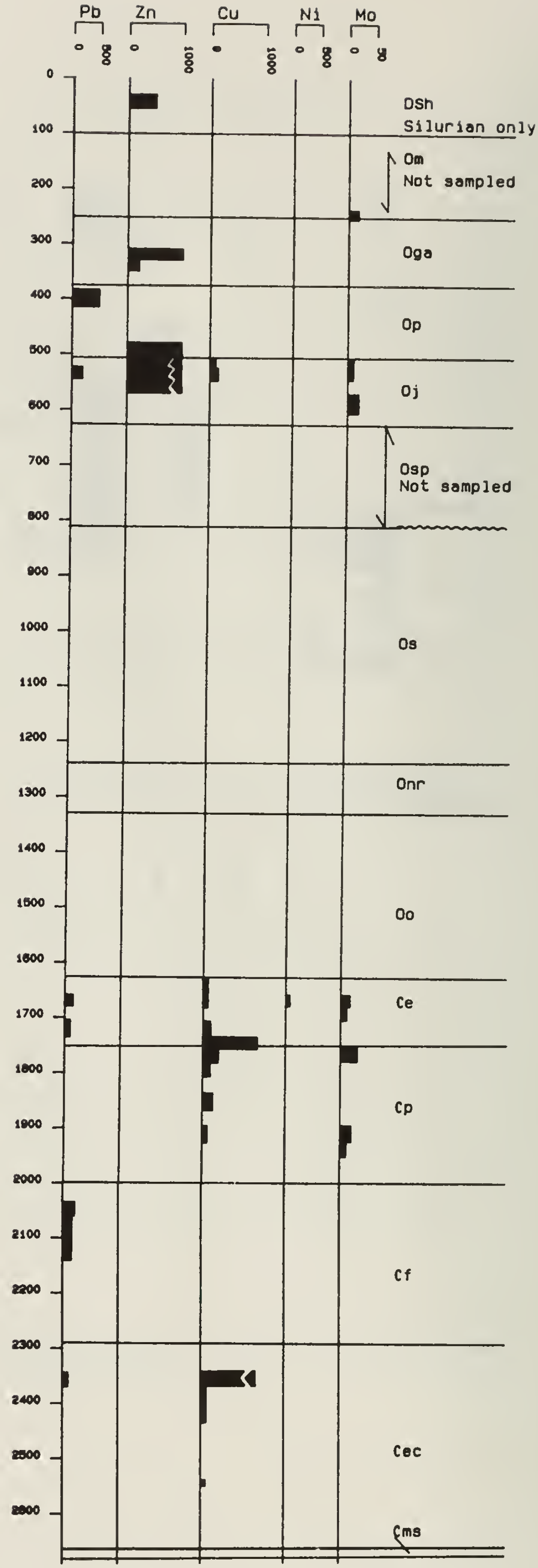
I-7: total depth 935 feet.



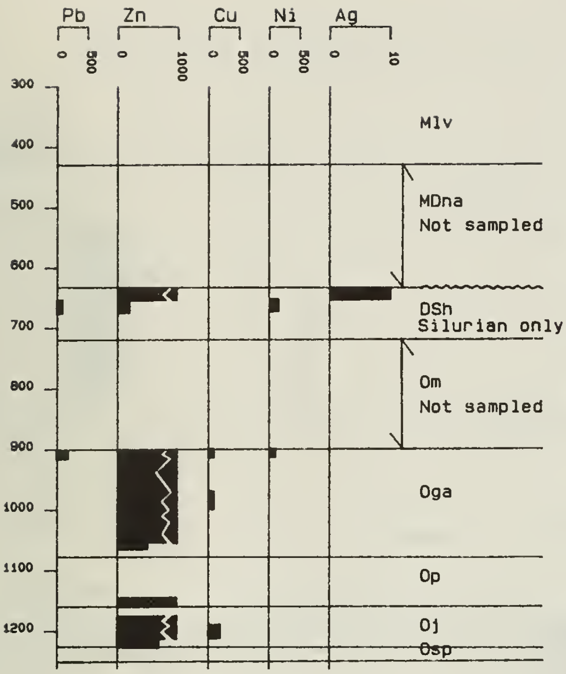
I-8: total depth 3025 feet. Sandstone from 2705 to 3025 feet was not sampled.



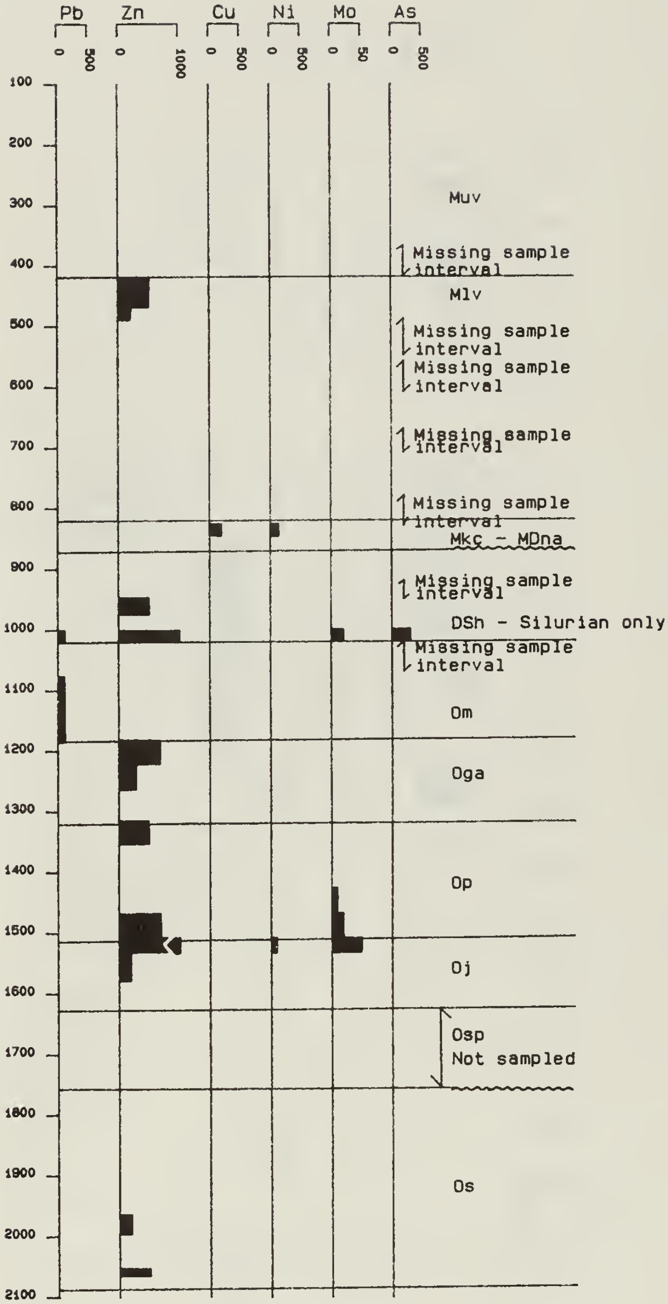
I-9: total depth 2226 feet. One sample of glauconitic siltstone in the Eau Claire formation from the interval between 2192 and 2216 feet contained no anomalous metal. Remainder of clastics from 2026 to 2221 feet was not sampled. Precambrian at 2221 feet.



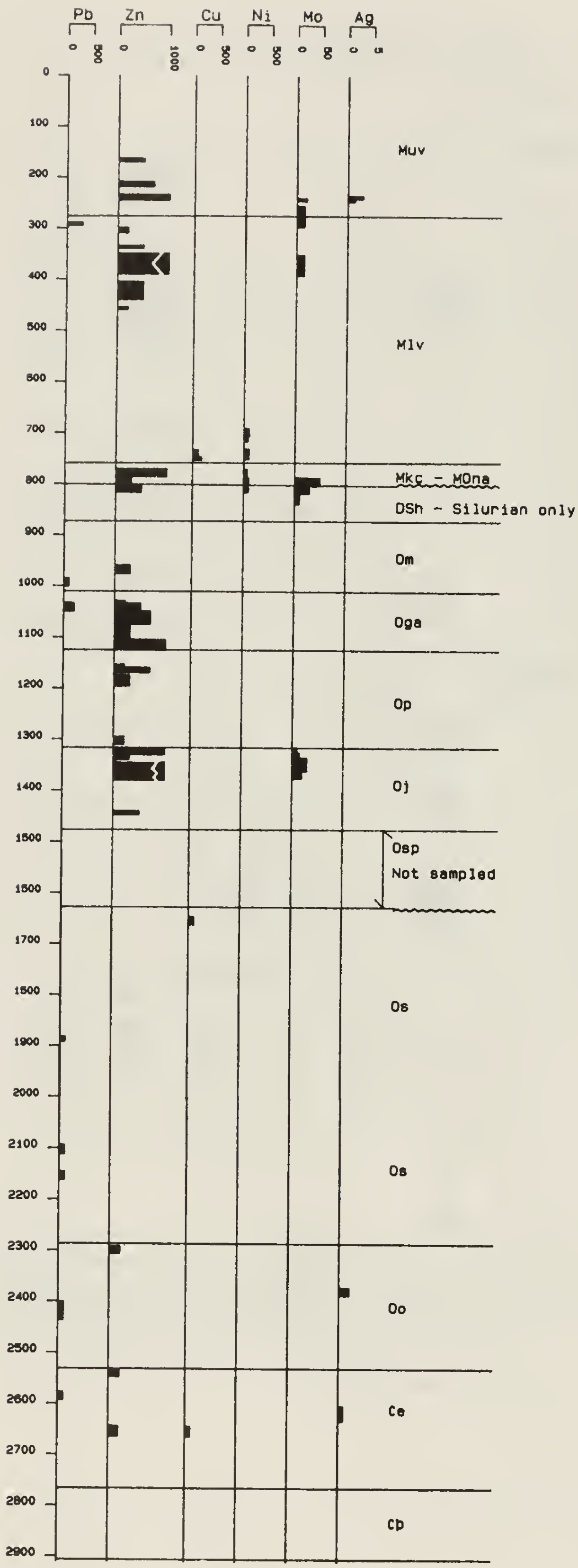
I-10: total depth 2680 feet.



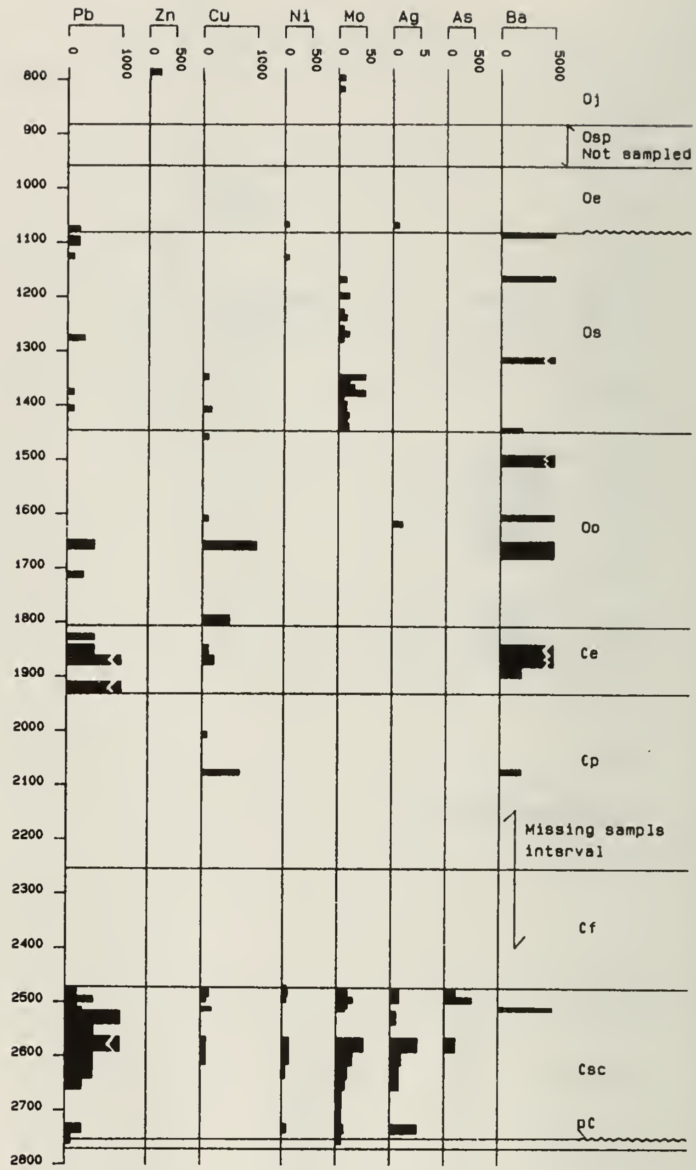
I-11: total depth 1247 feet.



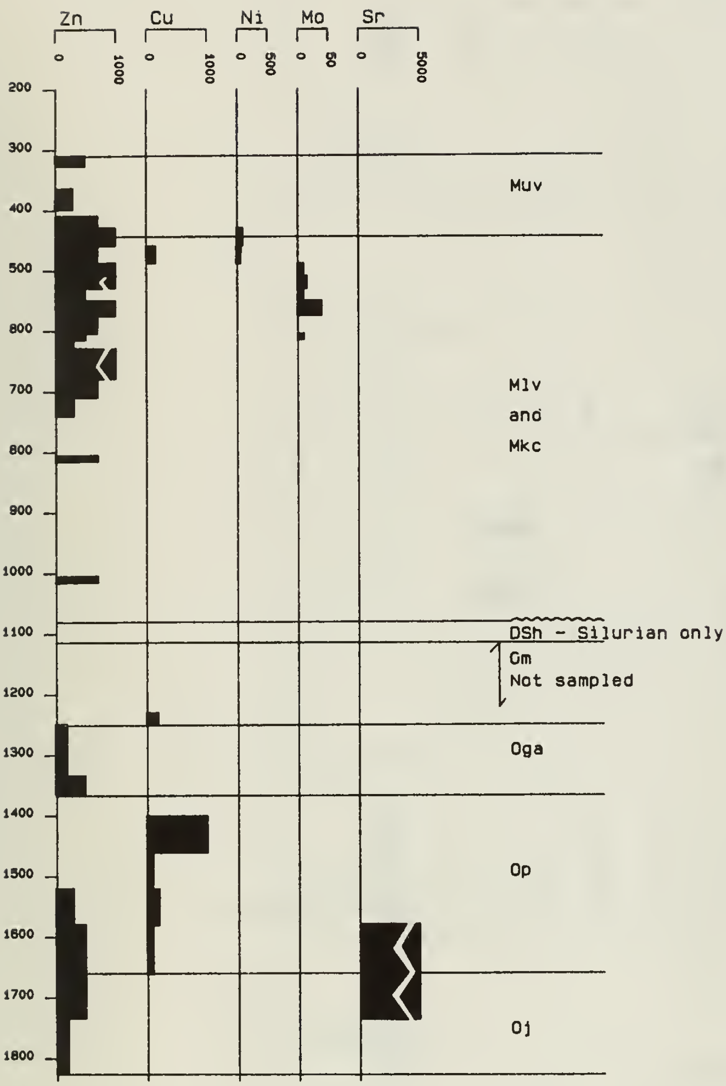
I-12: total depth 2085 feet.



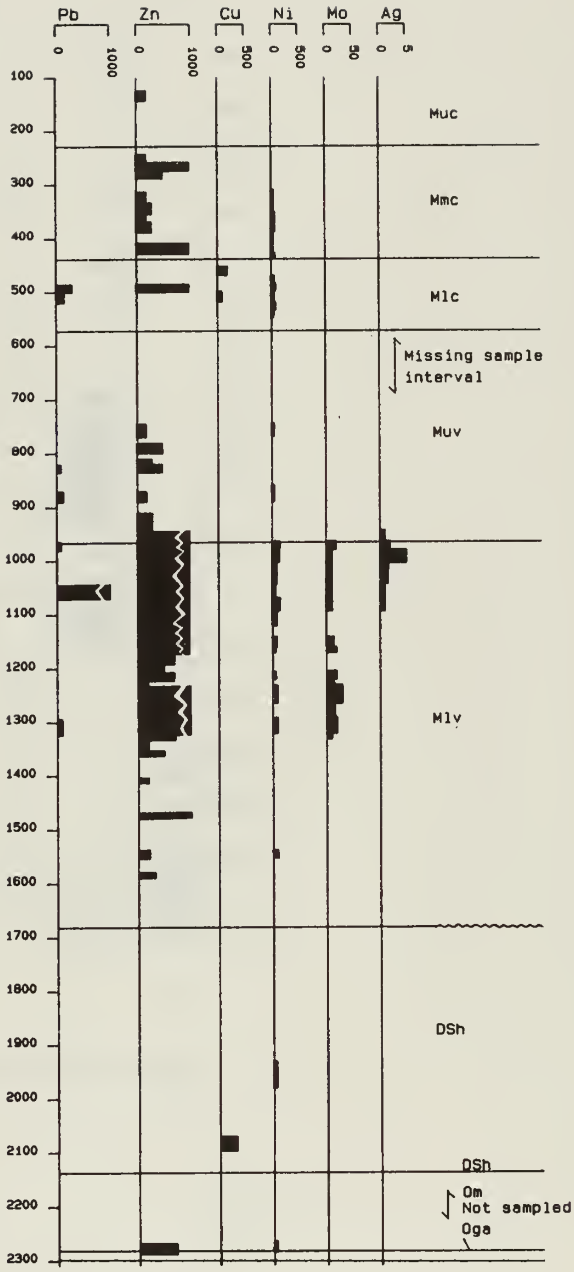
I-13: total depth 2904 feet.



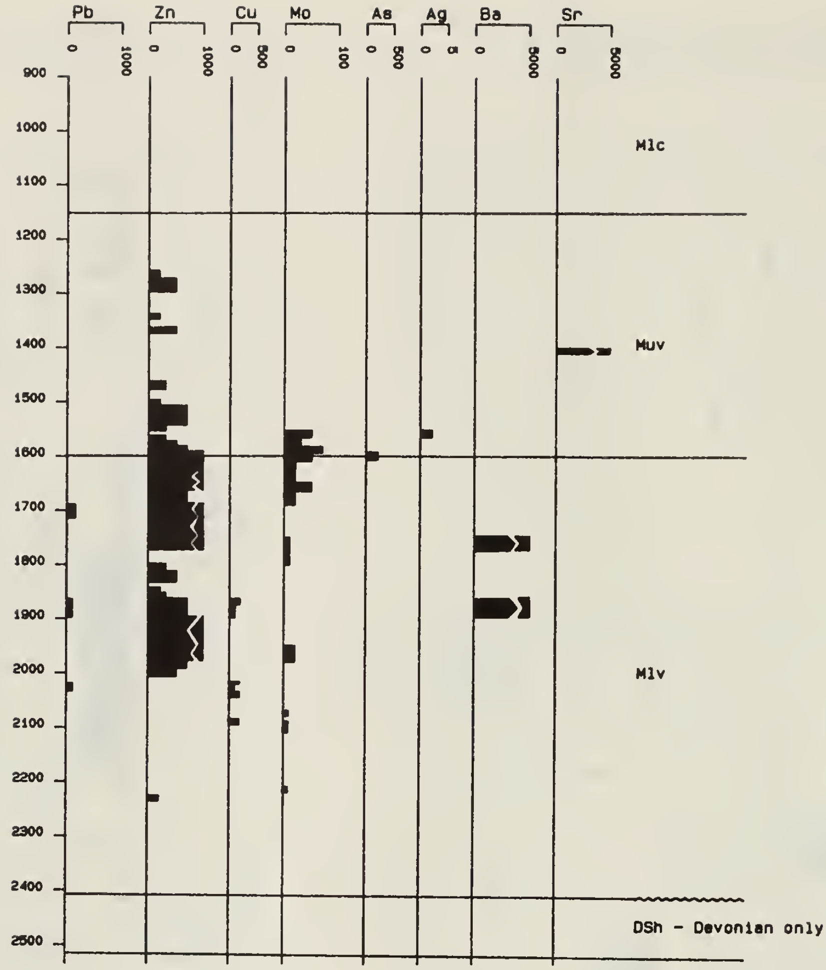
I-16: totai depth 2768 feet.



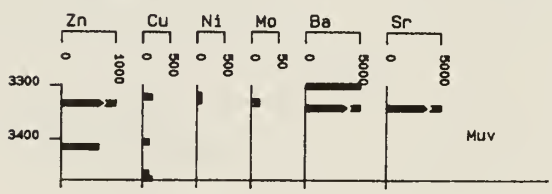
I-17: total depth 1910 feet. St. Peter sandstone from 1825 to 1910 feet were not sampled.



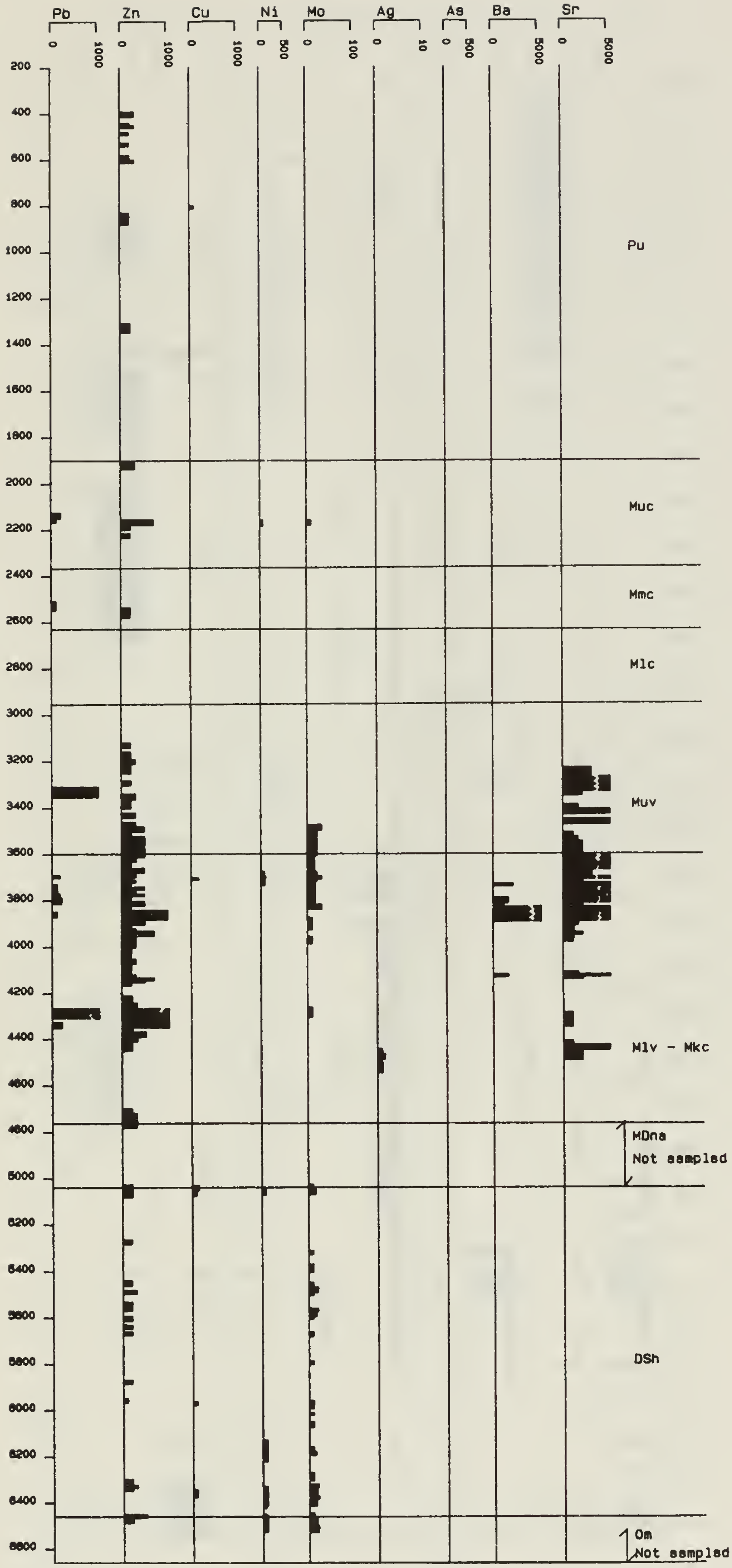
I-18: total depth 2300 feet.



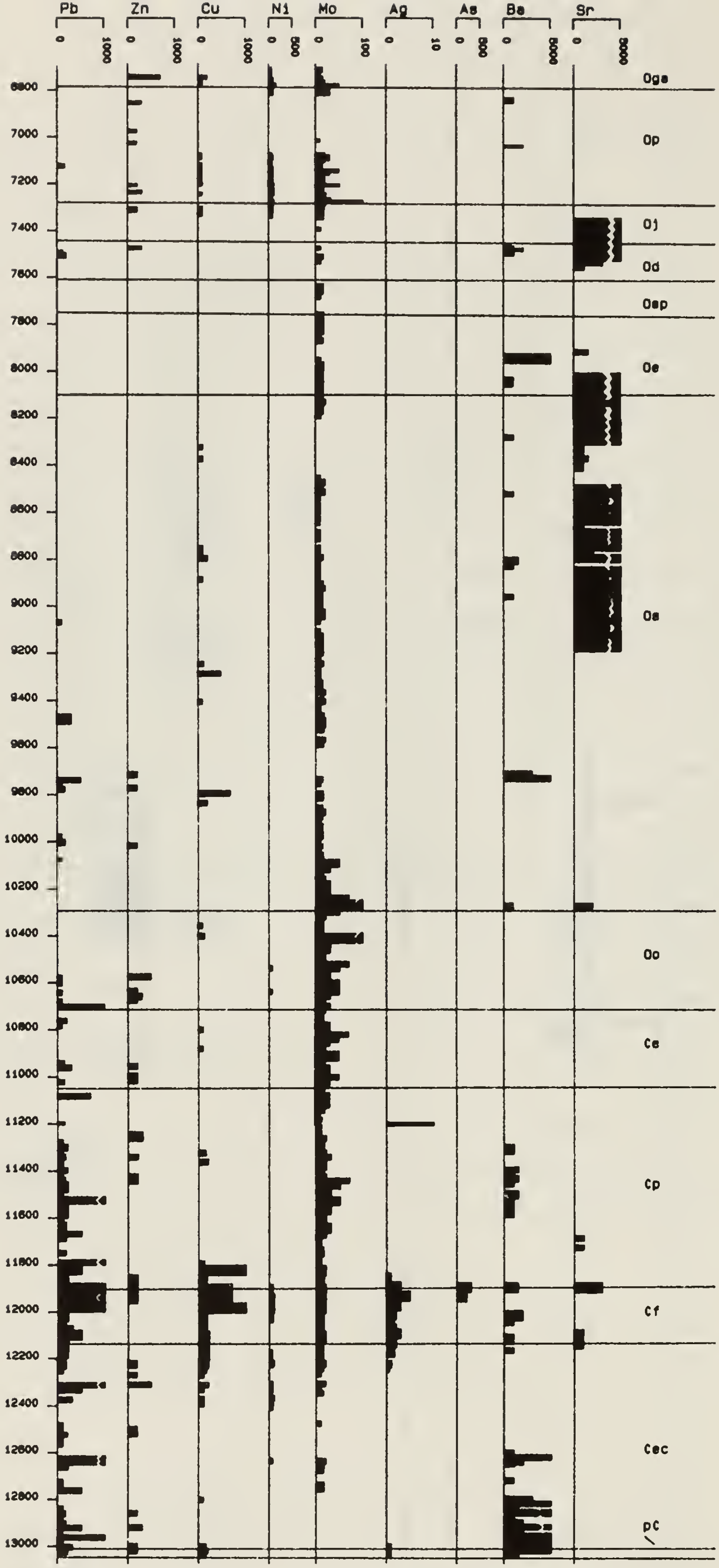
I-19: total depth 2519 feet.



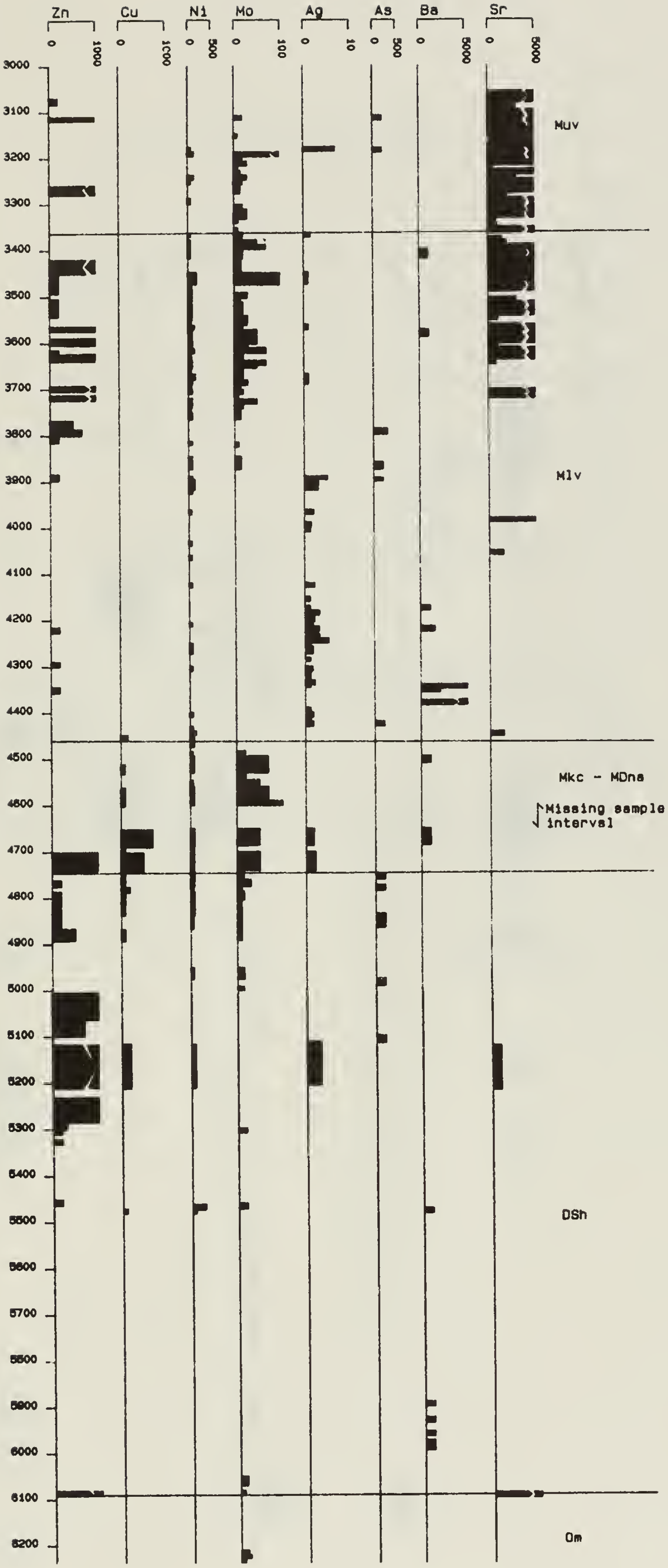
I-20: total depth 3477 feet.



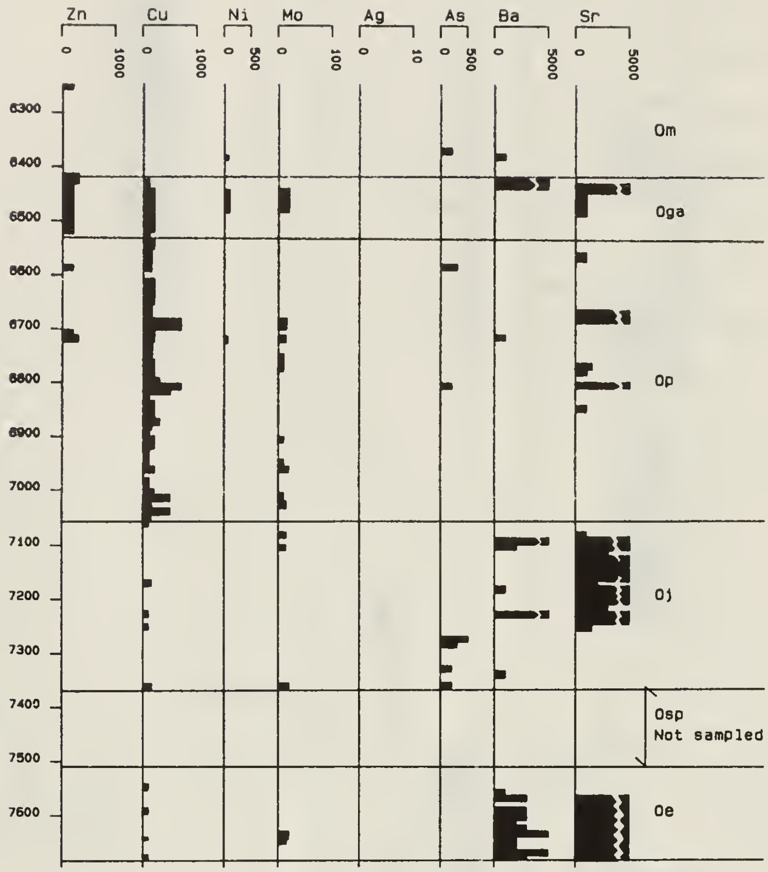
I-21: total depth 13051 feet.



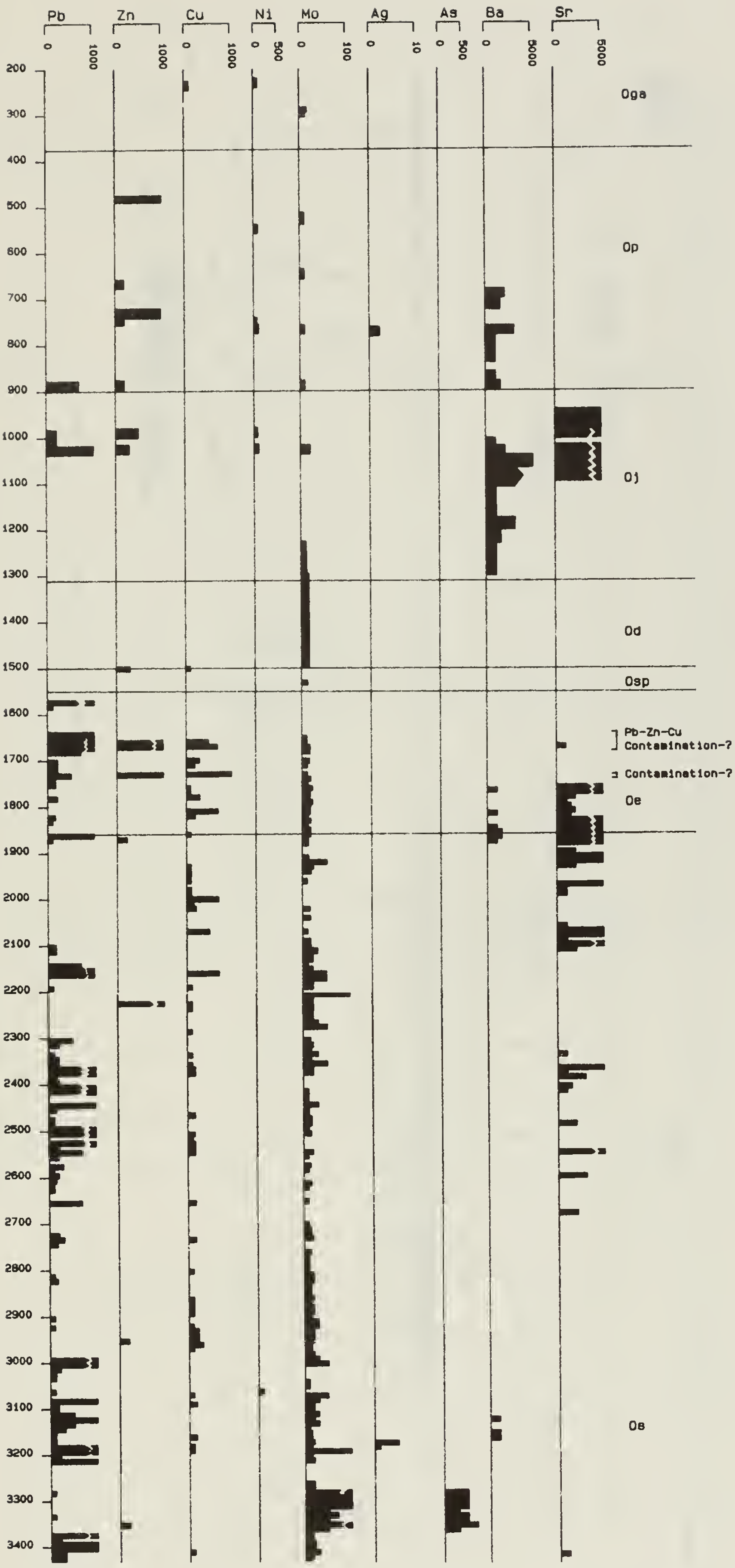
I-21 *(continued)*



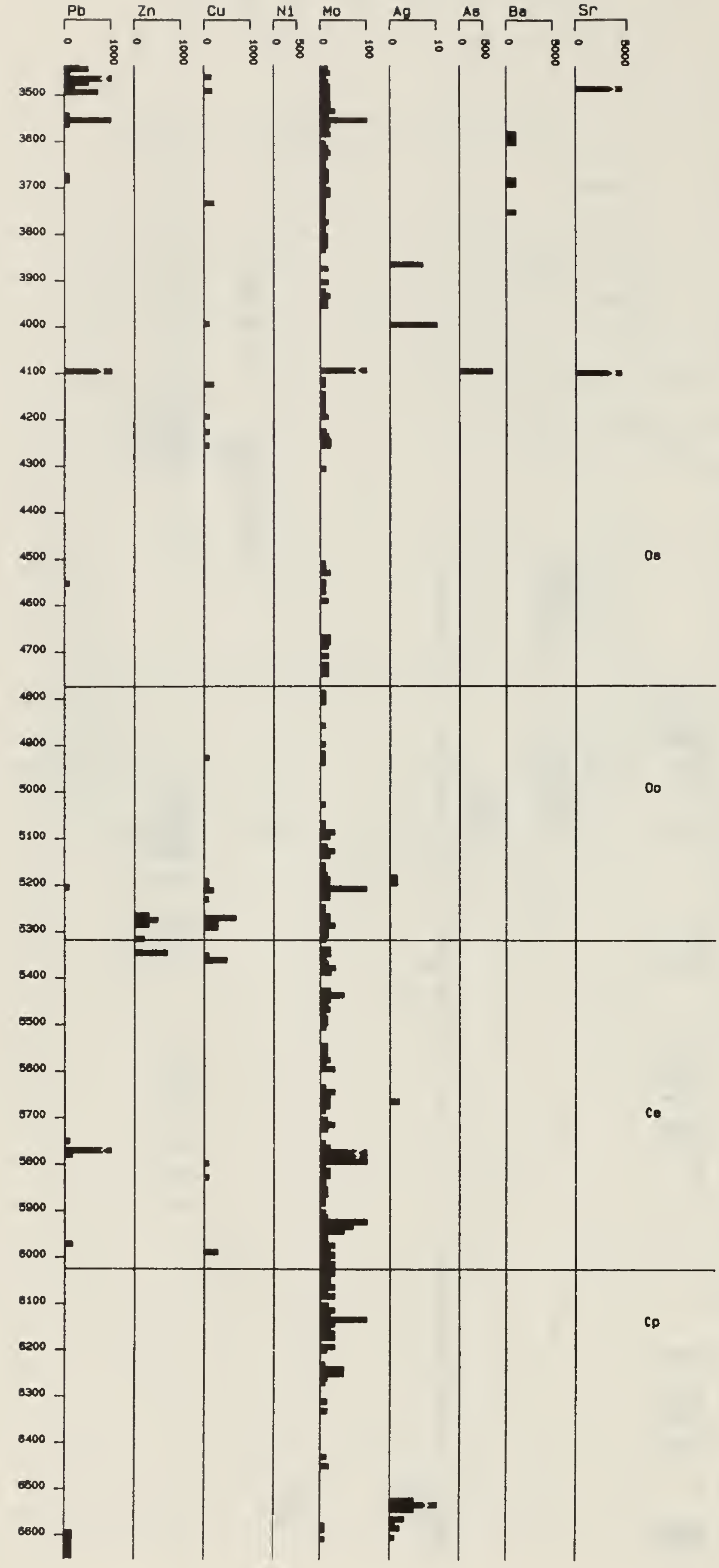
I-22: total depth 7683 feet.



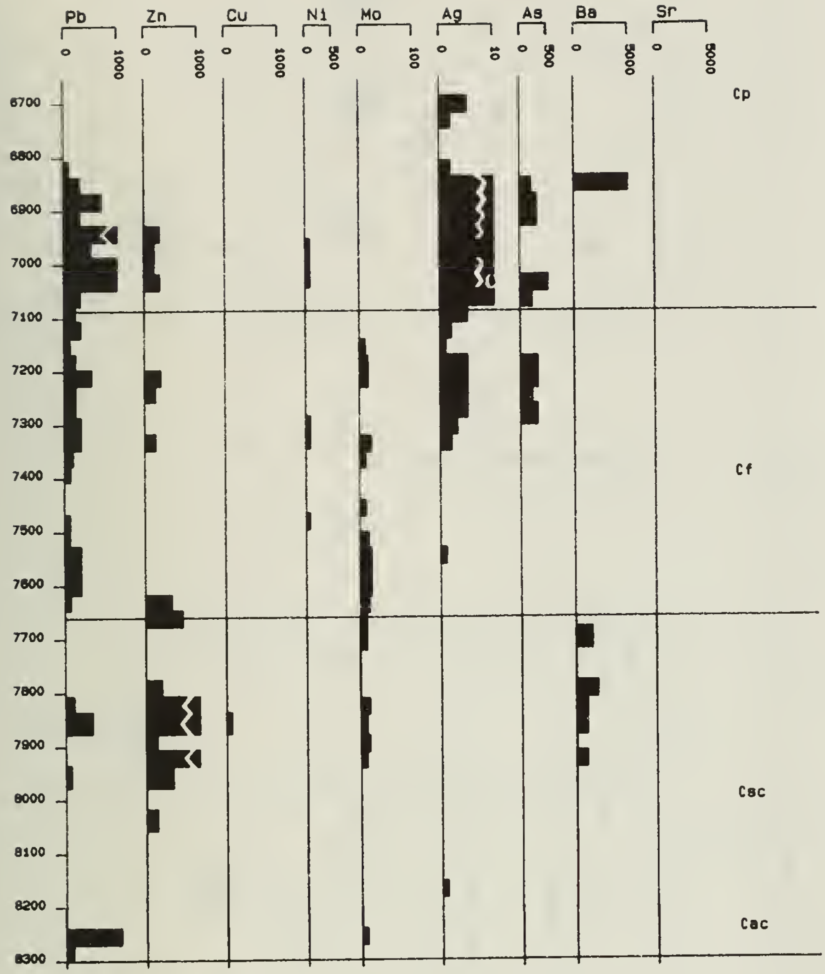
I-22 (*continued*)



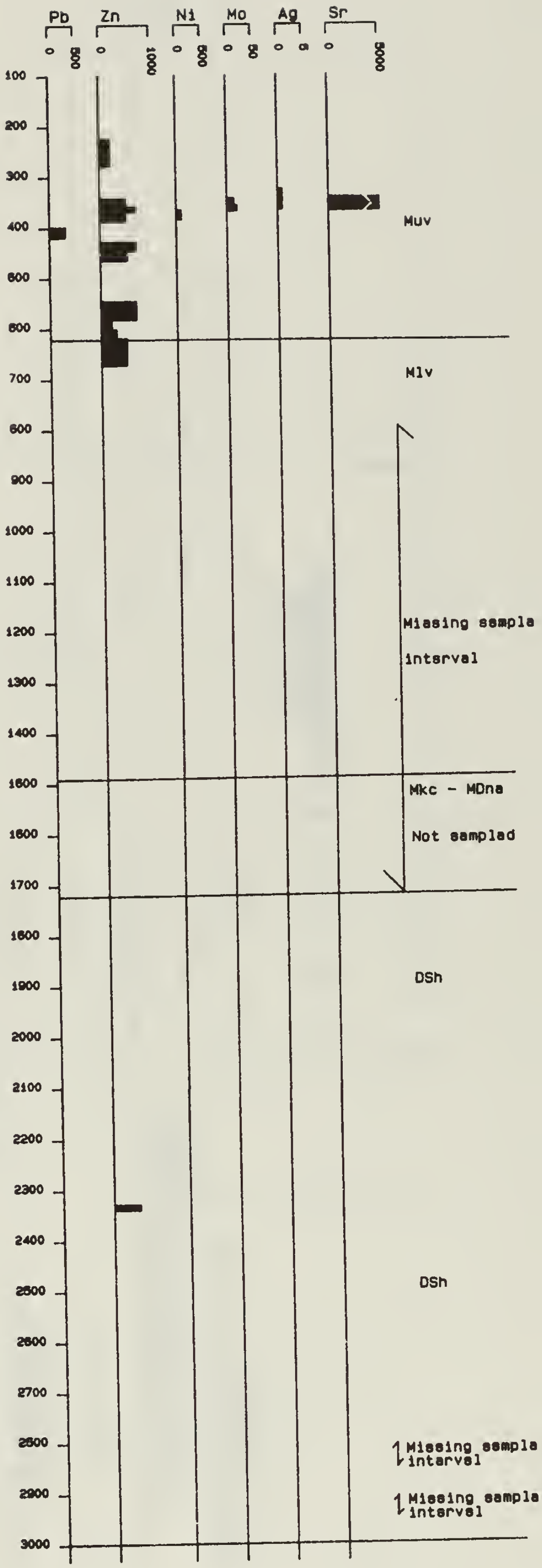
I-24: total depth 8492 feet. Sandstone from 8300 to 8492 feet not sampled.



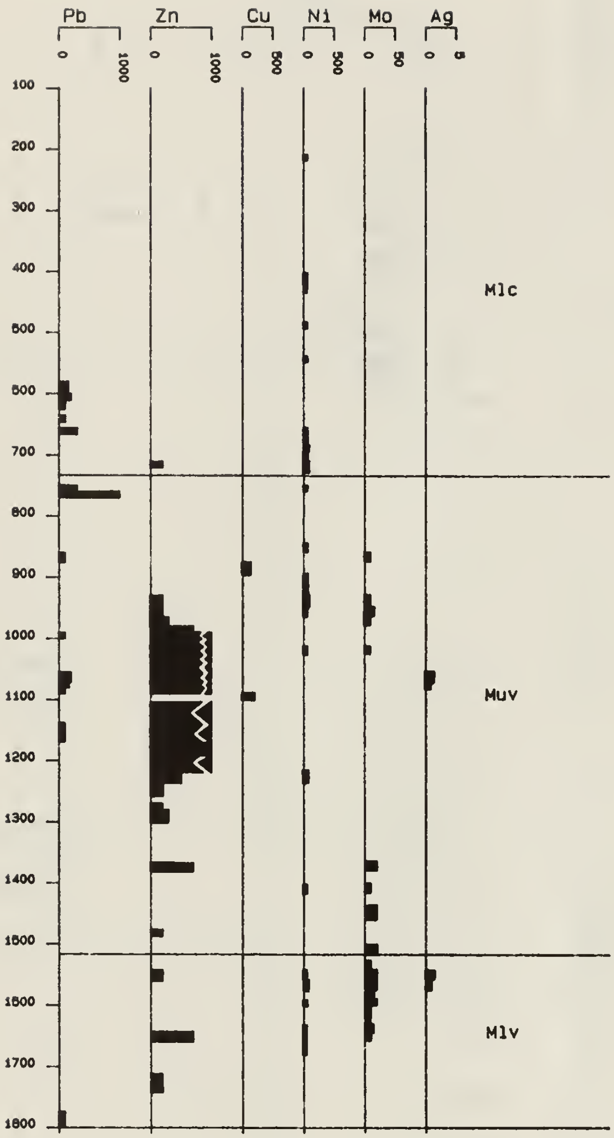
I-24 (*continued*)



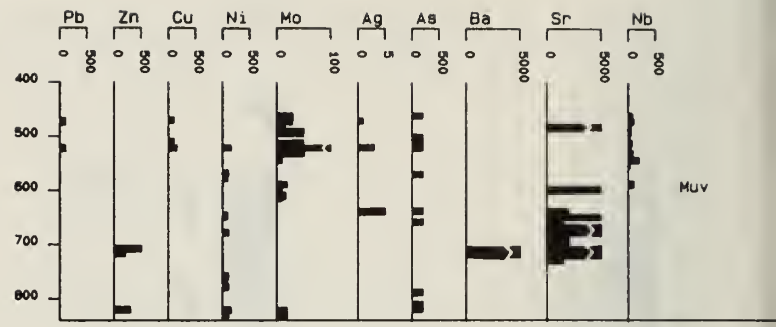
I-24 (*continued*)



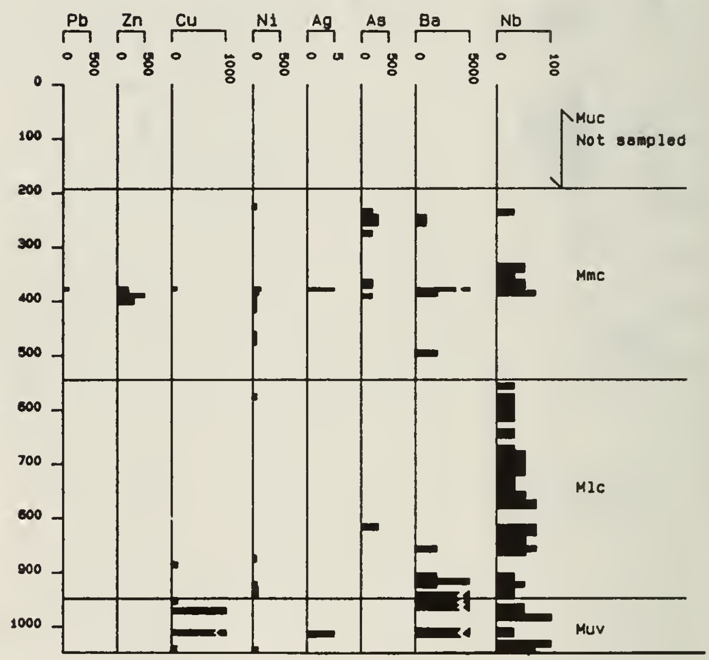
I-25: total depth 3022 feet.



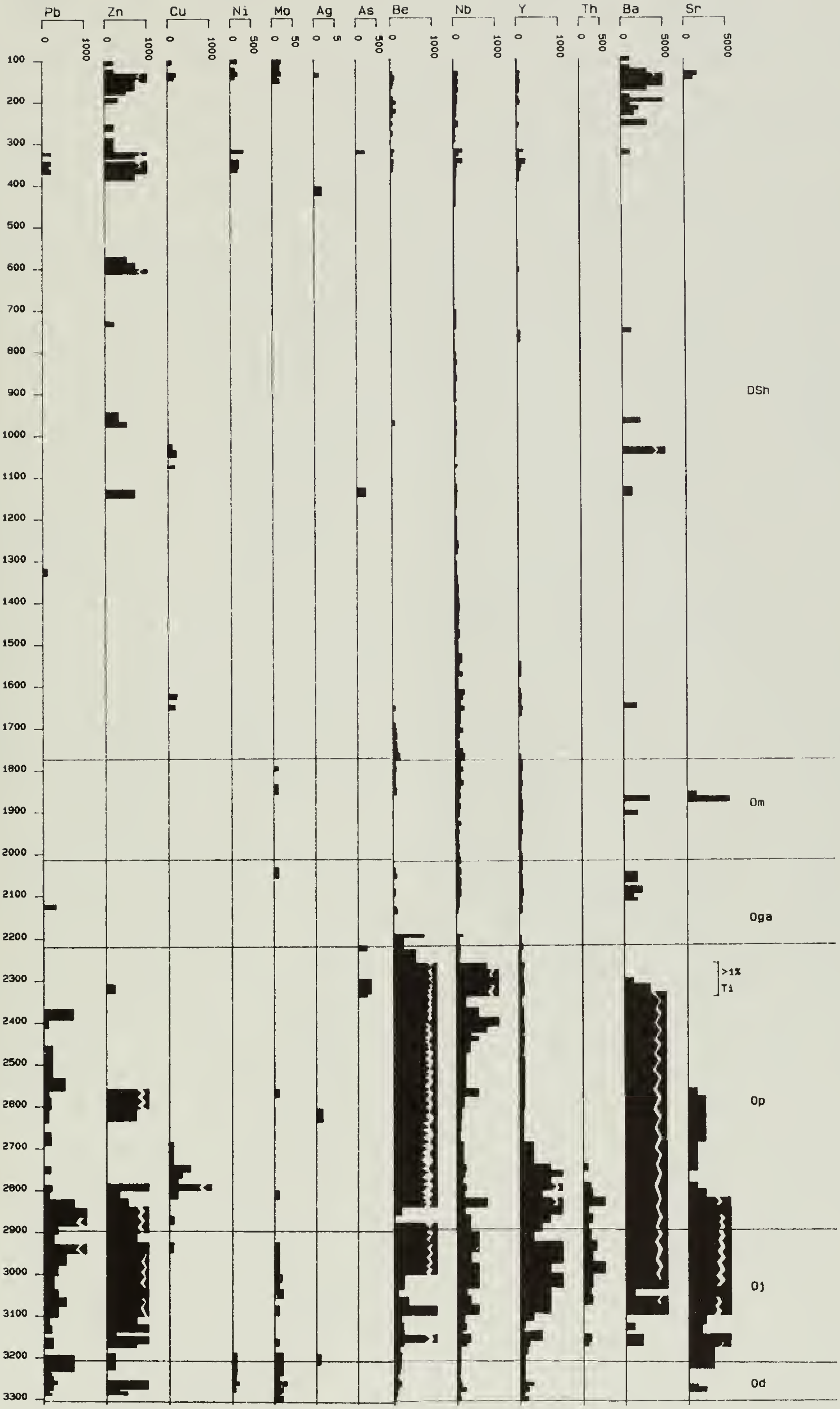
I-26: total depth 1800 feet.



I-27: total depth 834 feet.



I-28: total depth 1044 feet. Diamond drill core at angle of 56½° from horizontal (uncorrected).



I-29: total depth 3306 feet.